

Soret coefficient and the two-component Bénard convection in the benzene-methanol system

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When heated from below, layers of binary solutions with negative Soret coefficients present heating curves with characteristic shapes: A negative slope exists in the vicinity of the convection onset and a hysteresis appears. In the literature the values of the Soret coefficients for diluted solutions of methanol in benzene are generally reported as negative. In very carefully executed Bénard experiments with this system, we do not observe heating curves with such negative slopes. Our measurements, using convection in order to quantify the concentration gradients, are not in agreement with the reported Soret coefficient values.

INTRODUCTION

Usually, the Soret coefficients (D'/D) of binary-liquid mixtures are measured by heating a horizontal layer from above. The directed downward thermal density gradient should not induce convection currents. Some years ago, a linear hydrodynamic stability analysis of systems with both thermal and concentration gradients directed downward and upward was performed.^{1,2} The concentration gradient was induced by the thermodiffusion effect (Soret effect). We were interested in systems with negative D'/D and in that case, by definition, the denser component migrates toward the hotter side of the apparatus (i.e., the top of the cell in the "Soret configuration"). It was shown that a convection current may occur when a critical temperature difference (ΔT^{crit}) is exceeded. This may occur even if the total vertical density gradient is downward. The system, which is stable with respect to hydrostatic considerations, may be-

come unstable, due to dynamic properties of the thermal and concentration fluctuations, the relaxation time of concentration fluctuations being 100 times larger than the relaxation time of thermal fluctuations (typically the Prandtl number $N_{Pr}=10$ and the Schmidt number $N_{Sc}=1000$). This phenomena is generally called double diffusion instability. The critical temperature difference may be expressed as a dimensionless quantity by the critical Rayleigh number (N_{Ra}^{crit}), whose values depend not only on the thermal properties of the system, but also on its solutal properties, and particularly on the Soret coefficient values.

On the other hand, it has been pointed out by Schechter, Velarde, and Platten² that Soret coefficient values of benzene-methanol solutions have been measured by six independent groups of researchers³⁻⁸ by heating solutions from the top ("Soret configuration"). These results are reported in Table I. Let us remark that these results widely differ for diluted solutions in methanol in the case where

TABLE I. Soret coefficient values reported in the literature as a function of the molar fraction M of methanol in benzene.

M_{meth}	D'/D (K^{-1})					
	Tichacek ^a (Ref. 3) (40°C)	Prigogine ^b (Ref. 8) (20°C)	Thomaes (Ref. 4) (23.5°C)	Whitaker (Ref. 7) (35°C)	Tyrrell (Ref. 5) (25°C)	Turner (Ref. 6) (25°C)
S			10^7	5×10^3	10^4	150
0.1		0	-8×10^{-5}	...	-5.17×10^{-3}	-9.5×10^{-3}
0.2	-5.75×10^{-3}	$+4.68 \times 10^{-3}$	-6.5×10^{-5}	...	-4.90×10^{-3}	-6.5×10^{-3}
0.3			-3.5×10^{-5}	...	-3.86×10^{-3}	-3×10^{-3}
0.4		$+6.62 \times 10^{-3}$	$+1 \times 10^{-5}$	0	-2.89×10^{-3}	0
0.5	-4.79×10^{-4}		$+19 \times 10^{-5}$		-1.64×10^{-3}	$+2 \times 10^{-3}$
0.6		$+6.55 \times 10^{-3}$	$+25 \times 10^{-5}$	$+2.43 \times 10^{-3}$	-7.72×10^{-4}	$+3.5 \times 10^{-3}$
0.7			$+27 \times 10^{-5}$		0	$+4.4 \times 10^{-3}$
0.8	$+2.56 \times 10^{-3}$	$+5.87 \times 10^{-3}$	$+29 \times 10^{-5}$	$+2.99 \times 10^{-3}$	$+7.72 \times 10^{-4}$	$+4.2 \times 10^{-3}$
0.9			$+31 \times 10^{-5}$		$+2.18 \times 10^{-3}$	$+4 \times 10^{-3}$

^aPorous diaphragm cell.

^bThermogravimational method (horizontal temperature gradient).

D'/D is negative.

According to Ref. 2, the results of the different workers follow a pattern such that the ones with the largest values of S (a parameter proportional to $\Delta T d^3$, where d is the depth of the liquid layer) report the smallest Soret coefficients. This could be understood if one admits that the rest state of this system becomes unstable and that, above a critical value N_{Ra}^{crit} , the convection velocities are increasing functions of $N_{Ra} - N_{Ra}^{crit}$. These currents partly generated by the induced concentration gradient destroy it more or less efficiently.

These double diffusive instabilities are of importance in very different fields such as meteorology, solar energy, high-quality crystal production, oceanography, production of pure medication, separating living cells by electrophoresis, etc. As an example, the quality of the single crystals produced from melts are limited by chemical and structural inhomogeneities. The defect generation depends on heat and mass transfers during solidification. These fluxes are mainly governed by the convection movements of the liquid phase during processing. Furthermore, thermosolutal convection can be oscillatory.

RESULTS

Some years ago, we developed an apparatus with which accurate measurements of both heat flux and temperature in liquid-mixture horizontal layers could be taken. In particular, we studied organic compound solutions⁹ and aqueous solutions of methanol, ethanol,¹⁰ and isopropanol.¹¹ The last liquid mixtures have negative Soret coefficients in some ranges of concentration. In contradistinction with the Soret coefficient measurement configuration, our system is heated from below. In this case negative D'/D systems are stabi-

lized by the induced concentration gradient (i.e., the denser component migrates toward the hotter side, toward the bottom of the cell in this "Bénard configuration").

The plots of the temperature differences between the horizontal plates versus the heat flux (Schmidt-Milverton plots) have characteristic shapes due to the Soret effect and the double diffusion instabilities: In the vicinity of the critical point they present a region with a negative slope. It has been proved that this method is very sensitive. The increase of the critical temperature difference [$\Delta(\Delta T^{crit})$] and the negative slope segment are clearly visible without any possible ambiguity, as is shown in the inset to Fig. 1 and which is related to the water-methanol system.¹⁰ This method uses the convection onset as a measurement of the concentration gradient.

In order to understand and clarify the proposition of Schechter and co-workers² we undertook determination of Soret coefficients in diluted solutions of methanol in benzene by using our "Bénard configuration" apparatus. The experimental cell, described elsewhere,¹² is mainly composed of two heat-conducting horizontal plates. They are machined in copper and have 20 cm diameters. The temperature of the upper plate is efficiently held constant by a high flux of constant-temperature water flowing in a special heat exchanger. The temperature differences between the two plates can be accurately measured using platinum resistors (100 Ω at 0°C) and a precision Mueller bridge. The heat flux is imposed by an electrical heater whose power is carefully controlled and measured. The whole apparatus is placed in an insulated box whose temperature is controlled and kept constant with an accuracy better than 0.1°C and equal to the temperature of the cold wall (25°C). Using the results of the linear hydrodynamic stability theory, and the numerical value given by Tichacek, Kmak, and Drickamer,³ i.e., $-6 \times 10^{-3} \text{ K}^{-1}$, we have estimated that the increase of

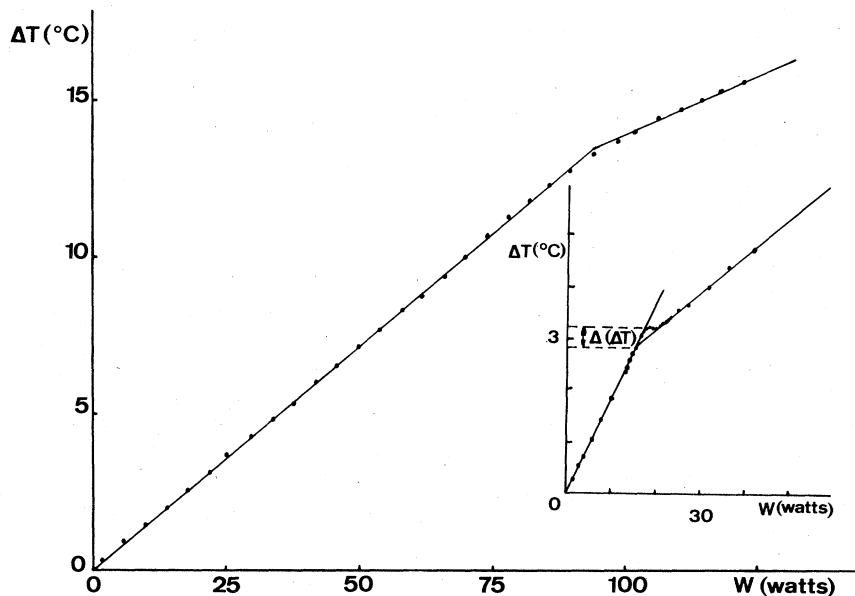


FIG. 1. Schmidt-Milverton plot for the benzene-methanol system. The mole fraction of benzene is 0.903, depth 0.87 mm, $\Delta T^{crit} = 13^\circ\text{C}$. The inset shows the water-methanol system (Ref. 10), where the weight fraction of water is 0.90, depth of the liquid layer 3.13 mm, $\Delta(\Delta T^{crit}) = 0.4^\circ\text{C}$.

Ra^{crit} (or ΔT^{crit}) should be equal to 6%. In the experiment, the results of which are reported in Fig. 1, the depth of the layer is 0.87 mm and the measured critical temperature difference is around 13 °C. From our estimations, the stabilizing effect due to the induced concentration gradient should be of the order of 0.8 °C. Such an important effect could not be missed. The results of our measurements do not reveal any stabilizing effect.

We have performed six runs of experiments in the entire range of concentration and with different layer depths. None of them indicate the existence of a negative Soret coefficient effect.

CONCLUSION

The Soret coefficient of diluted methanol solution in benzene could be negative or positive. If it is negative we have to admit that its absolute value must be much smaller than the previously reported values, at least 100 times smaller, producing a stabilizing effect of less than 1%, which could not be detected by our heat flux measurements. If it is pos-

itive then this result is surprisingly in contradiction with most of the values reported in the literature.

This system will be studied in the Soret coefficient measurement apparatus that we are preparing for the Eureka 1 mission in 1988. On this high-altitude free-flying platform, under very good microgravity conditions, we shall determine accurately the Soret coefficient of 24 different systems. This experiment will last for three months. The concentration gradient establishment will be followed in real time from Earth using the measurement of the induced emf of silver electrodes in the aqueous $AgNO_3$ solution system. The environment of the apparatus will guarantee the complete lack of convection of the liquid phase without any gaseous phase, in order to avoid any Marangoni convection.

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