# INFINITE-DILUTION ACTIVITY COEFFICIENTS BY COMPARATIVE EBULLIOMETRY: A MODEL OF EBULLIOMETER AND THE EXPERIMENTAL EQUIPMENT AND PROCEDURE

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The ebulliometric technique for determination of infinite-dilution activity coefficients is examined. A simple mathematical model of ebulliometer is formulated to derive and analyze corrections accounting for the difference between the composition of the ebulliometer charge and that of the equilibrium liquid. Our own experimental equipment employing the comparative ebulliometric setup is described along with the measuring procedure and calibration. Error analysis is carried out identifying major factors limiting the accuracy of the determination.

The principle of the ebulliometric determination of limiting activity coefficients consists[1] in measuring the boiling temperature at constant pressure or the equilibrium pressure at constant temperature as a function of the gravimetrically determined composition of dilute solutions. Using relations of classical thermodynamics, limiting activity coefficients can be calculated from these measurements without any assumption concerning the liquid-phase nonideality. For an isobaric experiment, which is usually preferred for its facility, one can derive[2,3]

$$\gamma_1^\infty = \frac{\varepsilon_1^\infty P_2^s}{P_1^s} \left[ 1 - \beta \left( \frac{\partial T}{\partial x_1} \right)_P^\infty \right], \tag{1}$$

where

$$\varepsilon_1^\infty = \exp \left[ \frac{(B_{11} - v_1^L)(P_2^s - P_1^s) + \delta_{12} P_2^s}{RT} \right]$$

$$\beta = \left( 1 + P_2^s \frac{B_{22} - v_2^L}{RT} \right) \frac{\mathrm{d} \ln P_2^s}{\mathrm{d} T}$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} .$$

Here, $P_i^s$ and $v_i^L$ are the pure-component vapor pressures and liquid molar volumes, respectively, and $B_{ii}$, $B_{ij}$ are the second virial coefficients. The quantity to be evaluated from the ebulliometric experiment is $(\partial T/\partial x_1)_P^\infty$, the limiting composition derivative

of the boiling temperature at constant pressure. However, a serious problem is encountered here (and in general always when applying the ebulliometry to mixtures) following from the fact that the gravimetrically determined composition $x_1^0$ of the ebulliometer charge does not correspond to the composition $x_1$ of the equilibrium liquid phase. Apparently, this is partly due to splitting the total stream to those of vapor and liquid, partly due to holdups in these streams. Thus correct mixture data can be obtained from ebulliometric measurements only if appropriate corrections for the effects mentioned are applied.

The purpose of this paper, which is intended to serve as an introduction to further papers presenting measured data on a wide variety of systems, is threefold:

*1*. To analyze the above-mentioned problem associated with the application of ebulliometry to mixtures by means of a simple mathematical model of ebulliometer.

*2*. To describe our experimental equipment, procedure and calibration.

*3*. To carry out error analysis.

*Model of Ebulliometer*

To derive and discuss the corrections accounting for the difference between the overall composition $x_1^0$ and the equilibrium liquid composition $x_1$, a mathematical model of ebulliometer is needed. We propose a simple model given schematically in Fig. 1. The total stream of a composition $x_1^F$ and a flow rate $\dot{n}_F$ is distributed inside the equilibrium chamber EC to the vapor-phase and liquid-phase streams in the evaporation ratio $f = \dot{n}_V/\dot{n}_L$, where $\dot{n}_V$ and $\dot{n}_L$ stand for the flow rates of the vapor phase and the liquid phase, respectively. The vapor-phase holdup, $n_V$, comprises the noncondensed
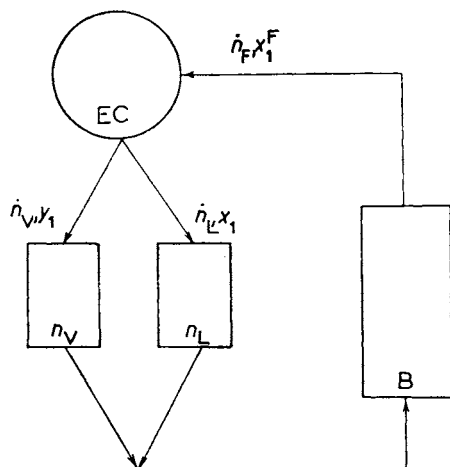


Fig. 1

Model of the ebulliometer. EC equilibrium cell, B boiler

vapor in the equilibrium chamber and, in the main, the condensate in the cooler and tubing. The liquid-phase hold up, $n_L$, is caused by the presence of a film of the equilibrium liquid on the thermometer well and on the walls of the equilibrium chamber. Both the flow rates and the evaporation ratio depend on the amount of heat delivered to the boiler. Fortunately, experience suggests[4,5] that $f$ remains fairly constant if the flow rate of vapor-phase condensate is kept constant, which can be readily indicated by means of a drop counter. Thus, on condition that the measurements are made for constant number of drops per a time unit, $f$ is a roughly constant characteristic of ebulliometer. The model just outlined may be considered as a synthesis of two still simpler models which have appeared in literature, namely of that considering explicitly the influence of the evaporation ratio only[4] and that assuming the vapor-phase holdup only[6−8].

To derive the relation between the composition of equilibrium liquid phase $x_1$ and the overall composition $x_1^0$ of the mixture charged into the ebulliometer, material balance equations are employed. For the number of moles of component 1 we can write

$$n_1 = y_1 n_V + x_1 n_L + x_1^F(n - n_V - n_L), \qquad (2)$$

where $n$ denotes the total number of moles in the ebulliometer. From the balance equations for the knot of the equilibrium chamber

$$\dot{n}_F = \dot{n}_V + \dot{n}_L \qquad (3)$$

$$x_1 \dot{n}_F = x_1 \dot{n}_L + y_1 \dot{n}_V \qquad (4)$$

combined with the definition of the evaporation ratio, $f = \dot{n}_V/\dot{n}_L$, the composition of total stream can be expressed as

$$x_1^F = \frac{f y_1 + x_1}{f + 1}. \qquad (5)$$

Substituting Eq. (5) into (2) and defining the relative holdups, $N_V = n_V/n$ and $N_L = n_L/n$, we get

$$x_1^0 = y_1 N_V + x_1 N_L + \frac{f y_1 + x_1}{f + 1}(1 - N_V - N_L). \qquad (6)$$

In addition to $f$, the relative holdups, $N_V$ and $N_L$, are regarded in the following as characteristic constants of ebulliometer considering that the amount of the ebulliometer charge changes very slightly during the experimental run.

When measuring the dependence of boiling temperature on the overall composition of the ebulliometer charge, the slope evaluated is $(\partial T/\partial x_1^0)_P^\infty$. Nevertheless, the required slope, $(\partial T/\partial x_1)_P^\infty$, may be obtained if a correction factor $(\partial x_1^0/\partial x_1)_P^\infty$ is

applied

$$\left(\partial T/\partial x_1\right)_P^\infty = \left(\partial T/\partial x_1^0\right)_P^\infty \left(\partial x_1^0/\partial x_1\right)_P^\infty \,. \tag{7}$$

On expressing the correction factor from Eq. (6), we get

$$\left(\partial x_1^0/\partial x_1\right)_P^\infty = \alpha_{12}^\infty N_V + N_L + \left(1 - N_V - N_L\right)\frac{f\alpha_{12}^\infty + 1}{f + 1}\,, \tag{8}$$

where

$$\alpha_{12}^\infty = \left(\partial y_1/\partial x_1\right)_P^\infty \tag{9}$$

is the relative volatility at infinite dilution for which we can also write

$$\alpha_{12}^\infty = \gamma_1^\infty P_1^s / \varepsilon_1^\infty P_2^s \,. \tag{10}$$

Combining Eqs (7), (8), and (10) with (1), we obtain the explicit equation for the activity coefficient at infinite dilution

$$\gamma_1^\infty = \frac{\varepsilon_1^\infty P_2^s}{P_1^s} \frac{f + 1 - \beta(\partial T/\partial x_1^0)_P^\infty \left(1 - N_V + N_L f\right)}{f + 1 + \beta(\partial T/\partial x_1^0)_P^\infty \left(f + N_V - N_L f\right)}\,. \tag{11}$$

For known values of the characteristic ebulliometer parameters, Eq. (11) makes it possible to calculate $\gamma_1^\infty$ directly from $(\partial T/\partial x_1^0)_P^\infty$ measured.

### Effects of $f$, $N_V$, $N_L$, and $\alpha_{12}^\infty$ on the Magnitude of the Correction

To examine the effects of characteristic ebulliometer parameters and system type on the magnitude of the correction reflecting the difference between $x_1$ and $x_1^0$, we define the quantity

$$\tilde{R} = \gamma_1^\infty/\hat{\gamma}_1^\infty \,, \tag{12}$$

where $\gamma_1^\infty$ denotes the correct value of the limiting activity coefficient as calculated from Eq. (11), and $\hat{\gamma}_1^\infty$ stands for the value we obtain on ignoring the difference between $x_1$ and $x_1^0$

$$\hat{\gamma}_1^\infty = \frac{\varepsilon_1^\infty P_2^s}{P_1^s}\left[1 - \beta\left(\frac{\partial T}{\partial x_1^0}\right)_P^\infty\right]. \tag{13}$$

Utilizing Eqs (11), (13), and (10), we get for $\tilde{R}$

$$\tilde{R} = \frac{Q\alpha_{12}^\infty}{Q + \alpha_{12}^\infty - 1}\,, \tag{14}$$

where we denote $Q = \left(\partial x_1^0/\partial x_1\right)_P^\infty$ for the sake of brevity.

For a common ebulliometer, the values of $f$, $N_V$, and $N_L$ are of the same order of magnitude amounting typically to several hundreds. This conclusion may be reached for the holdups on the basis of an estimate considering the ebulliometer design and for the evaporation ratio on the basis of its direct measurement[4]. Comparable magnitudes of $f$, $N_V$, and $N_L$ allow us to judge their influence on the value of $\tilde{R}$ by means of the respective derivatives

$$\frac{\partial \tilde{R}}{\partial f} = \frac{\alpha_{12}^{\infty}(\alpha_{12}^{\infty} - 1)^2 (1 - N_V - N_L)}{(f + 1)^2 (Q + \alpha_{12}^{\infty} - 1)^2} \tag{15}$$

$$\frac{\partial \tilde{R}}{\partial N_V} = \frac{\alpha_{12}^{\infty}(\alpha_{12}^{\infty} - 1)^2}{(f + 1)(Q + \alpha_{12}^{\infty} - 1)^2} \tag{16}$$

$$\frac{\partial \tilde{R}}{\partial N_L} = - \frac{f\alpha_{12}^{\infty}(\alpha_{12}^{\infty} - 1)^2}{(f + 1)(Q + \alpha_{12}^{\infty} - 1)^2} . \tag{17}$$

The above-given relations immediately imply that $\partial \tilde{R}/\partial f$ and $\partial \tilde{R}/\partial N_V$ are positive, and thus the correct value $\gamma_1^{\infty}$ is greater than that we get on neglecting $f$ and $N_V$. The effect of the liquid-phase holdup is opposite but unsubstantial being two orders of magnitude less. Therefore, $N_L$ will be neglected in further treatment. Comparison of Eqs (15) and (16) shows that $\partial \tilde{R}/\partial f$ and $\partial \tilde{R}/\partial N_V$ differ just by a factor $(1 - N_V - N_L)/(1 + f)$ which is near to unity. Thus, the effects of $f$ and $N_V$ should be considered to be of similar importance. On the other hand, since $\partial \tilde{R}/\partial f \approx \partial \tilde{R}/\partial N_V$ holds within relatively broad bounds, it is virtually impossible to evaluate $f$ and $N_V$ from calibration measurements for their strong correlation. This fact also explains why the different approaches which appeared in literature (Rogalski and coworkers[4] vs Ochi and Lu[6], Eckert and coworkers[7], Olson[8]) may yield essentially the same and correct results on using an effective value for the respective ebulliometer parameter. As a matter of course, the effective value of the parameter is higher than its true value in order to account for that of the both influences that is not considered explicitly in the given approach. It should be stressed, however, that the model ignoring the effect of evaporation ratio is, in principle, unrealistic since it treats the ebulliometer as a static device. It leads to an incorrect conclusion encountered sometimes in literature[9] that, for ebulliometers with a sufficiently large charge, the difference between $x_1^0$ and $x_1$ vanishes, and no corrections are necessary. This, of course, is not true since the only effect suppressed in this way is that of the vapor-phase holdup, while that of the evaporation ratio (i.e. splitting the total stream into the streams of the equilibrium liquid and vapor) remains still significant.

The magnitude of the correction $\tilde{R}$ is affected in the decisive manner by the nature of the system studied. The relevant system property is the infinite-dilution relative

volatility $\alpha_{12}^{\infty}$. For $\alpha_{12}^{\infty} = 1$, it follows from Eqs (8) and (14) that $Q = 1$ and $\tilde{R} = 1$ regardless of the magnitude of the ebulliometer parameters. However, as illustrated in Figs 2 and 3, the magnitude of $\tilde{R}$ continuously increases with increasing departure of $\alpha_{12}^{\infty}$ from unity. It can be seen that the influence of $\alpha_{12}^{\infty}$ on $\tilde{R}$ is more significant for $\alpha_{12}^{\infty} < 1$. The figures may also give an idea concerning the order of magnitude of the correction one should expect. Even for well-designed ebulliometers, $f + N_V$ may reach values about 0·1. Then, for systems, where $1/2 < \alpha_{12}^{\infty} < 2$, the correction is within 5%, for systems with $\alpha_{12}^{\infty}$ about 5 or 1/5, one should allow for a correction of several tens of per cent, and for systems where $\alpha_{12}^{\infty} \approx 10$, the correction reaches the order of 100%. For $\alpha_{12}^{\infty} \approx 0·1$, the correction would amount to several hundreds of per cent. For still lower values of $\alpha_{12}^{\infty}$, neglecting the correction causes $\gamma_1^{\infty}$'s to get physically unreal values. In this case, however, $\tilde{R} < 0$ since $Q + \alpha_{12}^{\infty} - 1 < 0$.

*Experimental Equipment and Procedure*

The ebulliometric determination of limiting activity coefficients relies on accurate measuring the concentration dependence of boiling points of dilute solutions. With the aim to meet the
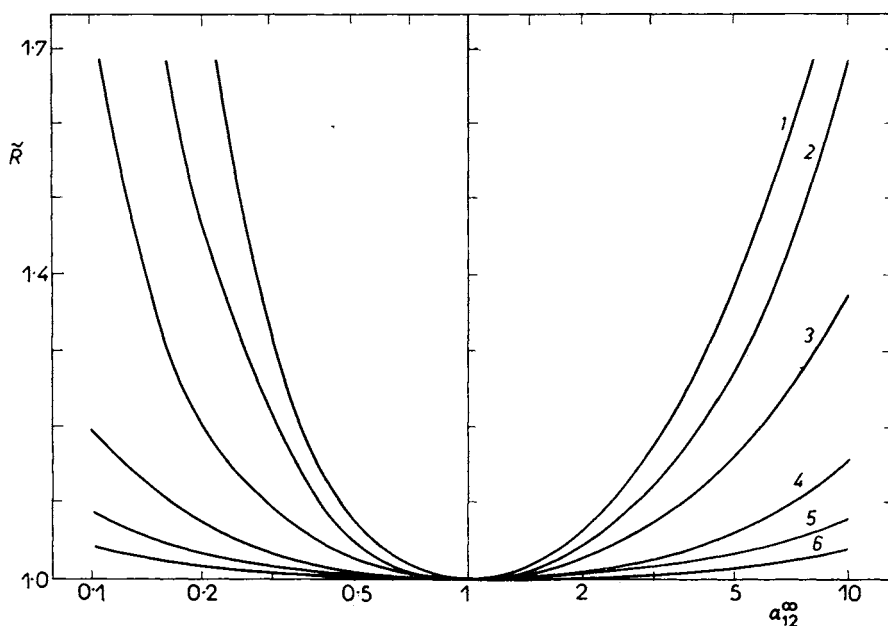


FIG. 2

Effect of $\alpha_{12}^{\infty}$ on $\tilde{R}$ for $N_V = N_L = 0$ and different values of $f$. *1* 0·15; *2* 0·1; *3* 0·05; *4* 0·02; *5* 0·01; *6* 0·005

requirement of high accuracy, we applied the technique of comparative ebulliometry. This technique consists in measuring the boiling temperature differences between the ebulliometer containing the mixture and that containing the pure solvent rather than in measuring the absolute boiling temperature. The experimental equipment and procedure we use is similar, though differs in details, to those recently described in literature[5−7,10−12].

Apparatus

Both the loading and reference ebulliometers are identical devices of the Swietoslawski type The loading ebulliometer is equipped with a feeding tube sealed with a suitable septum allowing a small amount of solute to be injected without interruption of boiling. The feeding tube is provided with an additional heating ensuring the whole amount of solute to be injected is transferred into the bulk circulating in the ebulliometer. Each of the ebulliometers is connected to a common, two-stage, on-off controlled manostatting system we have designed recently[13]. Here, a Texas Instruments quartz pressure gauge (Model 145) is used as the measuring device as well as the sensor for the pressure control. The reproducibility of the pressure measurement and setting amounts usually to a few Pa. The absolute accuracy is assumed to be $\pm 7$ Pa. The boiling temperatures and their differences are measured and monitored by a Hewlett–Packard quartz thermometer (Model 2801A) with two 2850A sensing probes and recorded by a digital
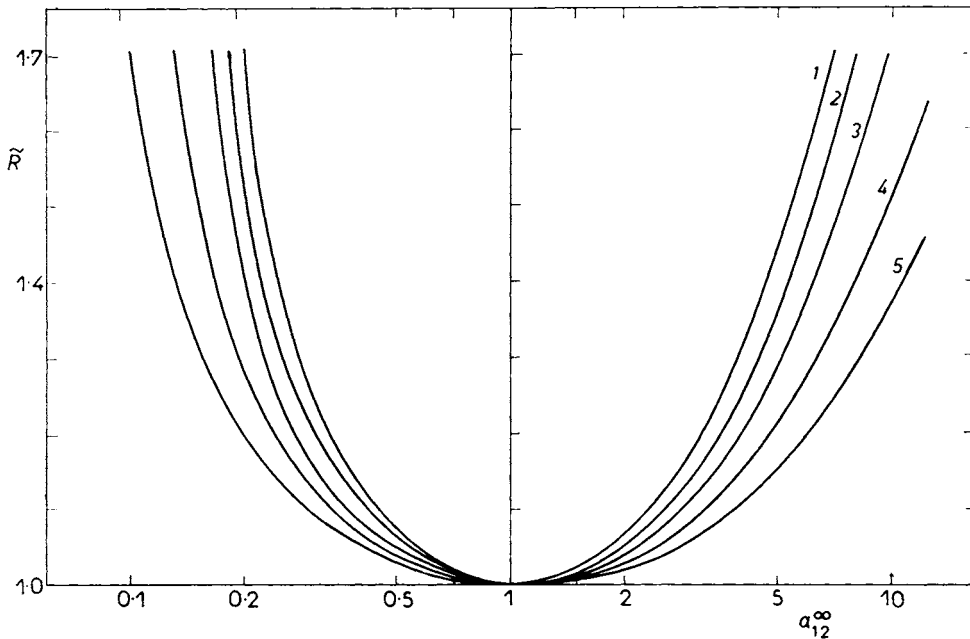


FIG. 3

Effect of $\alpha_{12}^{\infty}$ on $\tilde{R}$ for $f = 0.05$, $N_L = 0$ and for different values of $N_V$. *1* 0.1; *2* 0.075; *3* 0.05; *4* 0.01; *5* 0.0

printer. The thermometer makes it possible to measure directly the temperature difference between the loading and the reference ebulliometer thus taking full advantage of the comparative measurement. We calibrated the thermometer *in situ* by measuring vapor pressures of several dry organic solvents of high purity and this calibration was periodically rechecked. The reproducibility of the pure-component boiling point measurements usually amounted to a few mK, and the absolute accuracy is believed to be better than $\pm 0.02$ K. In typical cases, the measurement of boiling temperature differences is stable to $\pm 1$ mK.

### Procedure

The measuring ebulliometer was filled gravimetrically with solvent using a loading pipette. Roughly the same amount of the solvent (45—50 cm$^3$) was loaded into the reference ebulliometer. The equilibrium temperature difference between the ebulliometers, small in all cases, was recorded in every run to determine the zero offset. Then, a small amount (several tens of cm$^3$) of pure solute was injected gravimetrically into the loading ebulliometer through the serum septum with a gas-tight syringe. As soon as the steady state had been reached again (typically 10—15 min), the temperature difference was recorded again. Usually, six additions were made resulting in about 2 mol per cent concentration of solute.

The dependence of $\Delta T$ *vs* $x_1^0$ is in most cases well described by either of the following equations

$$\Delta T = \sum_{i=1}^{p} A_i (x_1^0)^i , \quad p = 1, 2, 3 \tag{18}$$

yielding for the desired limiting slope $(\partial T/\partial x_1^0)_P^\infty = (\partial \Delta T/\partial x_1^0)_P^\infty = A_1$. The parameters in Eq. (*18*) are determined by a least-squares method. To choose the appropriate representation, we take into account both the standard deviation of fit and the distribution of residuals.

### Calibration

As it has been stressed, the calibration equilibrium experiments enable us to evaluate only one of the characteristic ebulliometer parameters. Thus, two parameters must be fixed by other means. In view of the negligible influence of the liquid-phase holdup, we set $N_L = 0$. The vapor-phase holdup was estimated roughly as $N_V = 0.02$ considering the ebulliometer design. The uncertainty of such an estimate is sufficiently compensated by adjusting the remaining parameter $f$ from calibration measurements. The calibration was carried out through several systems exerting an enhanced departure of relative volatility from unity for which reliable and accurate $\gamma_1^\infty$ or $PTx$ data were available from the literature. The average value $f = 0.06$ and the standard deviation $s(f) = 0.015$ were calculated on the basis of eleven results obtained. Dependence of the correction factor $\tilde{R}$ on $\alpha_{12}^\infty$ for the values of parameters adopted for our loading ebulliometer is shown in Fig. 4. In this figure, the uncertainty $s(\tilde{R})$ caused by the inaccuracy in the evaporation ratio is also depicted. A reasonable agreement of $s(\tilde{R})$ with the uncertainties given in the literature for the data used for calibration implies correct performance of our experimental equipment and evaluation procedure.

### *Error Analysis*

A point of particular interest is the accuracy of ebulliometrically determined limiting activity coefficients. We can estimate it by means of the error propagation formula

$$s(\gamma_1^\infty) = \left[\sum_i (\partial\gamma_1^\infty/\partial a_i)^2 \, s^2(a_i)\right]^{1/2} , \qquad (19)$$

where $a_i$ are the input quantities for relation $(11)$, *viz.* the pure-component vapor pressures $P_1^s$, $P_2^s$; the virial coefficients $B_{11}, B_{22}, B_{12}$; the experimentally determined slope $(\partial T/\partial x_1^0)_P^\infty$, and the evaporation ratio $f$. Their standard deviations, $s(a_i)$, must be inferred from inaccuracies of their measurements or estimates. Concerning the pure-component vapor pressures, we have always measured their values using our equipment to avoid possible systematic errors due to impure substances or an artifice that might be caused by the adoption of incorrect literature values. Our experience with a number of substances suggests to set $s(P_1^s) = s(P_2^s) = 10$ Pa and $s(dP_2^s/dT) = 1$ Pa K$^{-1}$. For estimating virial coefficients the method by Hayden and O'Connell[14] is in common use. The inaccuracy of such estimates may be guessed as $s(B_{11}) = s(B_{22}) = 100$ cm$^3$ mol$^{-1}$ and $s(B_{12}) = 200$ cm$^3$ mol$^{-1}$. The given values represent a rather conservative estimate corresponding to cases where the method performs well. The standard deviation of $(\partial T/\partial x_1^0)_P^\infty$, $s(\partial T/\partial x_1^0)_P^\infty$, is found as the
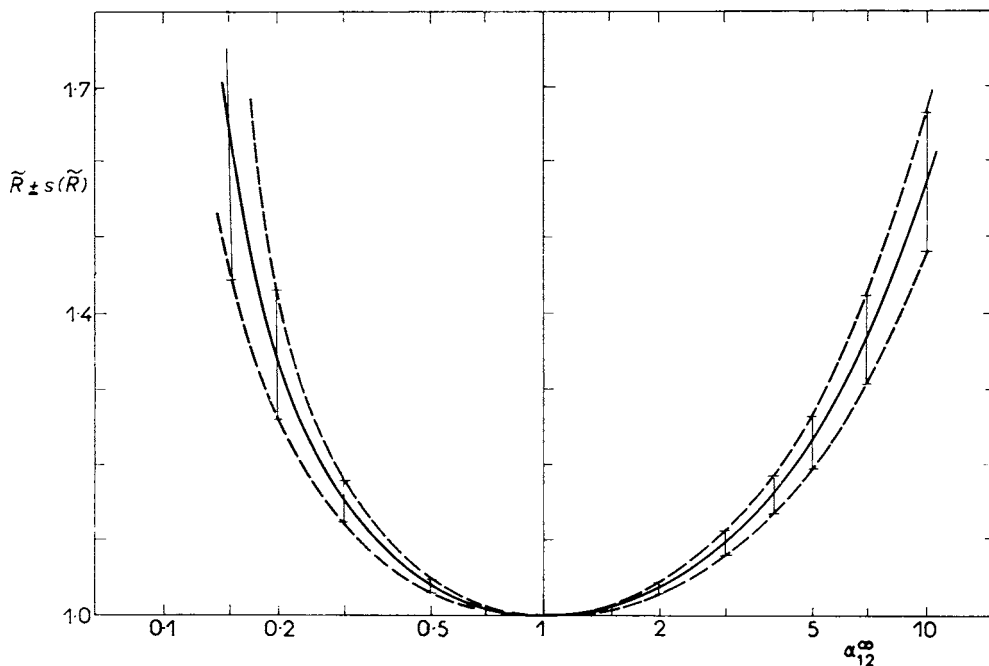


Fig. 4

Effect of $\alpha_{12}^\infty$ on $\tilde{R}$ and $s(\tilde{R})$ for our loading ebulliometer ($N_L = 0$, $N_V = 0.02$, $f = 0.06$, $s(f) = 0.015$); dashed curves mark the range $\pm s(\tilde{R})$

respective element of the variance-covariance matrix of parameters that is obtained as a by-product through the regression of $\Delta T - x_1^0$ data. As a rule, it amounts to $1 - 2\%$ of $(\partial T/\partial x_1^0)_P^\infty$.

Calculations on several dozens of systems we have examined so far show that the inaccuracies $s(P_1^s)$, $s(P_2^s)$, $s(\mathrm{d}P_2^s/\mathrm{d}T)$, and $s(B_{11})$ propagate negligibly to calculated value of $\gamma_1^\infty$. Relative importance of errors in the remaining input quantities depends on the system type. For systems with $\alpha_{12}^\infty$ not differing much from unity the largest error can arise from uncertainties in $B_{12}$ and $B_{22}$. The influence of the error in $f$ and, to a lesser extent, in $(\partial T/\partial x_1^0)_P^\infty$ becomes more important and gradually prevails for increasing departure of $\alpha_{12}^\infty$ from unity, which limits at last the applicability of the ebulliometric technique.

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