

**DETERMINATION OF THE ACTIVITY COEFFICIENTS  
IN THE ALIPHATIC ALCOHOL-NON-POLAR SOLVENT SYSTEMS**Jaromír HEJDA<sup>a</sup> and Věra JEDINÁKOVÁ<sup>b</sup><sup>a</sup> *Institute of Nuclear Fuels, 255 48 Prague 5-Zbraslav and*<sup>b</sup> *Department of the Nuclear Fuel Technology and Radiochemistry,  
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A method is proposed for the determination of the activity coefficients in aliphatic alcohol-non-polar solvent systems that are the main component of the organic phase in the boric acid extraction from aqueous solutions.

The knowledge of the activity coefficients of the equilibrium phase components is required for the evaluation of the extraction processes. The non-ideality of the organic phase is connected mainly with the processes of the extractant association, solvation with the solvent molecules and hydration of the organic phase components. The knowledge of the activity coefficients of binary systems is the first step for the evaluation of multicomponent solutions, including also the mutual interaction of components.

Methods for the determination of the concentration activity coefficients in binary systems are described in various monographs on the solution theory<sup>1-3</sup>. The evaluation of the activity coefficients of one component of the solution is based on the experimental determination of the other component activity. Cryoscopy, ebullioscopy, potentiometric titration and the measurement of the vapour pressure changes in a vapour osmometer are the methods most often used for the determination of the solvent activities in the extraction studies. After substituting the osmotic coefficient  $\varphi$  into the Gibbs-Duhem equation for the binary solution the evaluation of the activity coefficients  $\gamma_2$  of the solute is reduced to the solution of the equation

$$\ln \gamma_2 = (\varphi - 1) + \int_0^{m_2} \frac{\varphi - 1}{m_2} dm_2. \quad (1)$$

In this equation (and also throughout the whole paper) index 1 is used for the solvent and index 2 for the solute.

In this equation, as well as in all other considerations in this paper, the standard state of the solute based on the Henry law is used ( $a_2 \rightarrow m_2$  for  $m_2 \rightarrow 0$ ).

## EXPERIMENTAL

The data required for the evaluation of  $\varphi$  were obtained by the vapour osmometer Knauer at 25°C. The method is based on the determination of the vapour pressure difference of the solvent and solution. The difference of the electrical resistance  $\Delta R$  of thermistors is measured, which is proportional to the temperature difference of the solvent and solution drops. The method is described in detail elsewhere<sup>4-8</sup>. Burge<sup>8</sup> gives the following relation,

$$\Delta R = K\varphi m_2, \quad (2)$$

for the direct determinations of the molal osmotic coefficient  $\varphi$ , where  $K$  is a calibration constant of the apparatus. The solvent activity can be then obtained using the definition of the molal osmotic coefficient

$$\varphi = -\frac{m_1}{m_2} \ln a_1. \quad (3)$$

The solutions in toluene (analytical grade, Lachema) of the following aliphatic alcohols were measured: n-octanol (analytical grade, Lachema), n-decanol (pure, Lachema), n-dodecanol (pure, Reachim), 2-ethylhexanol (pure, Lachema). All these alcohols were purified by double rectification. The experimental data are presented in Table I.

The calibration constant of the vapour osmometer was determined by the measurement of a reference substance (benzil) using the relation

$$\lim_{m_2 \rightarrow 0} \frac{\Delta R}{m_2} = K. \quad (4)$$

## RESULTS

*Method for the Activity Coefficients Determination*

Solutions of aliphatic alcohols in non-polar solvents are characterized by a high association already at low molalities. The recalculation of the experimental data into a form suitable for the evaluation of activity coefficients, *i.e.*, into the dependence of  $(\varphi - 1)/m_2$  on  $m_2$ , shows that the curves steeply increase with the decreasing molality of the alcohol ( $m_2 \rightarrow 0$ ). The extrapolation to zero is therefore not reliable, particularly for alcohols with short chains. Therefore the graphical solution of the integral in Eq. (1) cannot be used.

Another solution of the problem is to use a suitable empirical function as an approximation of the experimental dependence  $(\varphi - 1) = f(m_2)$ . Along with the sufficiently precise fitting of the experimental points this function must be of such a type that after its substitution into the integral in Eq. (1) the primitive function can be found and the definite integral in the limits from pure solvent ( $m_2 = 0$ ) to the solution of the given molality  $m_2'$  can be evaluated.

It has been proved that the approximation proposed by Izmailov<sup>2</sup>,  $(\varphi - 1) = \beta m_2^\alpha$ , is not suitable for the experimental data of aliphatic alcohols in toluene.

Much better results were obtained with the polynomial  $(\varphi - 1) = am_2 + bm_2^2 + cm_2^3$ , that was used by Goldman for the cryoscopic data of nitrobenzene in benzene<sup>9</sup>.

The application of the polynomial regression on the system aliphatic alcohols-toluene is based on the fact that Eq. (4) is valid for the reference substance.

It is evident that all functions  $\Delta R = f(m_2)$ , determined under comparable conditions (the same temperature and solvent), approach in the limit the slope with the same value of  $K$ .

In order to obtain the best fitting of the experimental points, polynomials of various orders of the type

$$\Delta R = Km_2 + bm_2^2 + cm_2^3 + \dots, \quad (5)$$

or after substitution into Eq. (2)

$$\varphi - 1 = b'm_2 + c'm_2^2 + d'm_2^3 + \dots \quad (6)$$

TABLE I

Data of the vapour osmometer ( $\Delta R$ ) measured for the solutions of alcohols in toluene at 25°C

$m_2$ , mol kg <sup>-1</sup>	$\Delta R$	$m_2$ , mol kg <sup>-1</sup>	$\Delta R$
n-octanol		2-ethylhexanol	
0.0691	88.1	0.0818	103
0.1413	164	0.1526	177
0.3718	358	0.3709	356
0.6617	539	0.6280	524
0.6760	530	0.6851	561
1.054	704	1.070	758
1.407	848	1.378	855
1.475	859	1.411	920
2.197	1 090	2.139	1 180
n-decanol		n-dodecanol	
0.0600	99.8	0.0664	109
0.0985	151	0.1141	176
0.3304	377	0.1952	259
0.6029	570	0.3519	406
0.6739	599	0.6165	572
0.9992	772	1.311	927
1.366	928	1.783	1 110
1.615	1 040		

were used. It has been found that the experimental data for alcohols can be reasonably fitted only using polynomials with noninteger exponents, *e.g.*,

$$\Delta R = Km_2 + bm_2^{1.5} + cm_2^2 + \dots, \quad (7)$$

however, the calculated curves tend to oscillate between experimental points. In this case the mathematical criterion (*i.e.*, the sum of squares of the differences between the experimental and calculated values) cannot be used as the primary measure of the approximation correctness as the experimental errors are not smoothed. The correct shape of the calculated dependence is particularly important at low molalities, where the differences between the calculated values of the functions  $\Delta R = f(m_2)$  or  $(\varphi - 1) = f(m_2)$  and the experimental points reflect themselves substantially in the ratio  $(\varphi - 1)/m_2$  and therefore also in the value of the definite integral of Eq. (1). For these reasons the polynomial regression is not a suitable form of the solution and therefore another method of approximation was sought.

For systems with substantial positive deviation from the ideal behaviour (on the basis of the statistical theory of McMillan and Meyer) Zagorets<sup>10</sup> derived the following relation between the solvent activity coefficient in the scale of molar ratios  $f_1$  and the molality  $m_2$  of the solute

$$\frac{m_2^2}{\ln f_1} = A + Bm_2, \quad (8)$$

where  $A$  and  $B$  are constants. Substituting this expression into the Gibbs-Duhem equation for a binary system and using the relation

$$\ln a_1 = \ln X_1 + \ln f_1, \quad (9)$$

where  $X_1$  is the molar ratio, Ochkin<sup>11</sup> obtained after integration a relation

$$\ln \gamma_2 = -\frac{m_1}{B} \left[ \ln \left( 1 + \frac{B}{A} m_2 \right) + \frac{Bm_2}{A + Bm_2} \right], \quad (10)$$

that is appropriate for the direct evaluation of the solute activity coefficient at low molalities (lower than 0.025 mol kg<sup>-1</sup>). For the aliphatic alcohol-non-polar solvent solutions under study it has been found that the dependence of  $m_2^2/\ln f_1$  on  $m_2$  is linear up to the values of  $m_2$  about 1.5 mol kg<sup>-1</sup> so that in this interval it is possible to determine the values of the constants  $A$  and  $B$ . Eq. (8) was then adopted for the evaluation of the activity coefficients in the given systems using this procedure: Combining Eqs (2), (3), (9), and (8)  $\varphi$  can be expressed as a function of a single variable  $m_2$  (*i.e.*, without  $\Delta R$ ),

$$\varphi \equiv \frac{\Delta R}{K m_2} = -\frac{m_2 m_1}{A + B m_2} - \frac{m_1}{m_2} \ln \frac{m_1}{m_1 + m_2}. \quad (11)$$

Substituting Eq. (11) into the integral in Eq. (1) and after integration, the following relation is obtained

$$\int_0^{m_2'} \frac{\varphi - 1}{m_2} dm_2 = -\frac{m_1}{B} \ln \frac{A + B m_2}{A} - \ln \frac{m_1 + m_2}{m_2} + \frac{m_1}{m_2} \ln \frac{m_1}{m_1 + m_2} + 1. \quad (12)$$

The final expression for the evaluation of the activity coefficient  $\gamma_2$  has the form

$$\ln \gamma_2 = -\frac{m_1}{B} \left[ \ln \left( 1 + \frac{B}{A} m_2 \right) + \frac{B m_2}{A + B m_2} \right] - \ln \frac{m_1 + m_2}{m_1}. \quad (13)$$

The final relation (13) makes possible, in comparison with the published relation (10), to evaluate the activity coefficients for higher values of molalities that correspond or are close to the values in extraction systems.

#### *Activity Coefficients in the Systems Aliphatic Alcohols-Toluene*

Using the experimental values of  $\Delta R$  the values of the ratio  $m_2^2/\ln f_1$  were evaluated using the Eqs (2), (3), and (9) and plotted against  $m_2$  in a graph. Table II gives the values of the constants  $A$  and  $B$  determined for the linear parts of these curves, *i.e.*, up to the molality value  $1.5-2 \text{ mol kg}^{-1}$ . Table III that relates to *n*-octanol, gives together with the experimental values of  $\Delta R$  and  $\varphi$  also their values recalculated from Eqs (8), (9), (3), and (2) and denoted by  $\Delta R_{AB}$  and  $\varphi_{AB}$ . It is evident that at the lowest molality values the experimental values of  $\Delta R$  are subjected to a higher error that is more evident in the value of the osmotic coefficient  $\varphi$ . Using the function  $m_2^2/\ln f_1 = f(m_2)$  it is possible to eliminate the too deviated points and the calculated

TABLE II  
Values of the constants  $A$  and  $B$  for different alcohols

Compound	$A$	$B$
<i>n</i> -Octanol	2.470	15.68
2-Ethylhexanol	2.156	16.47
<i>n</i> -Decanol	4.373	15.52
<i>n</i> -Dodecanol	4.620	15.55

curve  $\Delta R_{AB} = f(m_2)$  correctly fits the experimental points. For other alcohols only the resulting activity coefficients are presented (Table IV) as determined by Eq. (13).

For the evaluation of the activity coefficients  $\gamma_2$  of aliphatic alcohols in the given range of molalities it is necessary to determine only two constants,  $A$  and  $B$ . This method of evaluation can be applied for an arbitrary system for which the dependence  $m_2^2/\ln f_1 = f(m_2)$  is linear.

TABLE III

Values of  $\Delta R_{AB}$ ,  $\varphi_{AB}$ , and the activity coefficients  $\gamma_2$  for the system n-octanol-toluene as a function of the molality  $m_2$  (in mol kg<sup>-1</sup>)

$m_2$	$\Delta R_{\text{exp}}$	$\varphi_{\text{exp}}$	$\Delta R_{AB}$	$\varphi_{AB}$	$\gamma_2$
0.0691	88.1	0.675	103	0.786	0.626
0.1413	164	0.614	178	0.666	0.457
0.3718	358	0.510	349	0.497	0.257
0.6617	539	0.431	515	0.412	0.172
0.6760	530	0.415	522	0.409	0.170
1.054	704	0.353	701	0.352	0.122
1.407	848	0.319	845	0.318	0.0970
1.475	859	0.308	870	0.312	0.0934
2.197	1 090	0.263	1 100	0.265	0.0670

TABLE IV

Values of the activity coefficients of alcohols in the systems (n-decanol, n-dodecanol, 2-ethylhexanol)-toluene as a function of the molality  $m_2$  (in mol kg<sup>-1</sup>)

$m_2$	$\gamma_2$	$m_2$	$\gamma_2$	$m_2$	$\gamma_2$
n-decanol		n-dodecanol		2-ethylhexanol	
0.0600	0.768	0.0664	0.760	0.0818	0.559
0.0985	0.671	0.1141	0.650	0.1526	0.416
0.3304	0.387	0.1952	0.524	0.3709	0.245
0.6029	0.264	0.3519	0.385	0.6280	0.172
0.6739	0.245	0.6165	0.270	0.6851	0.162
0.9992	0.184	1.3110	0.155	1.070	0.117
1.366	0.145	1.7830	0.121	1.378	0.0971
1.615	0.127			1.411	0.0953
				2.139	0.0685

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