TABLE 2. Heat of combustion of tetraethoxysilane.

| Mass of tetraethoxysilane, g | $W\Delta\theta$, cal | $q_f$, cal | $q_{HNO_3}$, cal | $q_C$, cal | $q_{Si}$, cal | $\Delta U^\circ$, cal g$^{-1}$ |
|---|---|---|---|---|---|---|
| First series of combustion experiments | | | | | | |
| 0.66026 | 5154.4 | 1019.6 | 0.8 | 29.0 | 22.0 | —6338 |
| 0.77553 | 6046.0 | 1247.0 | 2.4 | 115.2 | — | —6333 |
| 0.64879 | 4989.2 | 882.9 | 3.2 | 11.0 | — | —6341 |
| 0.73515 | 5748.3 | 1124.8 | 3.5 | 31.1 | — | —6327 |
| 0.48055 | 3942.6 | 896.0 | 1.3 | 9.4 | — | —6357 |
| | | | | | Mean | —6339±10 |
| Second series of combustion experiments | | | | | | |
| 0.63647 | 4633.5 | 617.0 | 1.6 | 25.4 | — | —6344 |
| 0.73036 | 5137.2 | 577.7 | 0.9 | 75.6 | — | —6345 |
| 0.80815 | 5636.9 | 595.9 | 1.2 | 81.9 | — | —6353 |
| 0.69603 | 4956.8 | 559.4 | 0.7 | 22.1 | — | —6349 |
| 0.71515 | 5092.0 | 611.8 | 1.0 | 66.9 | — | —6357 |
| | | | | | Mean | —6350±5 |

The average standard heats of combustion of triethoxysilane and tetraethoxysilane obtained from the second series of combustion experiments are greater than Reuther's values[1] by about 3 kcal mole$^{-1}$ and about 5 kcal × × mole$^{-1}$ respectively.

Reuther's low results[1] may be explained by the same factors which we mentioned at the beginning of this paper and by his failure to carry out a chemical analysis of the combustion products of the ethoxysilanes and make appropriate corrections for the incomplete combustion of carbon and silicon. Furthermore, Reuther did not have at his disposal a reliable method for the combustion of organosilicon compounds.

The authors thank S. I. Kleshchevnikova for providing the ethoxysilane specimens, V. N. Kostryukov for his interest in this work and valuable advice, and E. S. Lazarev for technical assistance.

## SUMMARY

1. The standard heats of combustion of tri- and tetra--ethoxysilanes have been determined.
2. An improved method for the combustion of organosilicon compounds with reliable chemical analysis of the combustion products has been described.

1. H.Reuther, Chem.Tech.(Berlin), 2, 331 (1950).
2. R.Thompson, J.Chem.Soc., 1908 (1953).
3. K.H.Birr and C.Sarafidis, Z.anorg.Chem., 311, 97 (1961).
4. K.H.Birr, Z.anorg.Chem., 315, 175 (1962).
5. V.L.Volkov, M.I.Kafyrov, *et al.*, Symposium "Plasticheskie Massy" (Plastics), Vol.12, Goskhimizdat, Moscow, 1962, p.28.
6. S.I.Kleshchevnikova, Ya.E.Pokrovskii, and E.I.Rumyantseva, Zhur.Tekh.Fiz., 27, 1645 (1957).
7. M.M.Popov, "Termometriya i Kalorimetriya" (Thermometry and Calorimetry), Izd.Moskov.Gos.Univ., 1953.
8. W.D.Good and D.R.Douslin, J.Phys.Chem., 63, 1133 (1959).
9. F.D.Rossini, J.Res.Nat.Bur.Stand., 33, 255 (1944).
10. A.P.Kreshkov (Editor), "Rukovodstvo po Analizu Kremnii-organicheskikh Soedinenii" (Manual of the Analysis of Organosilicon Compounds), Goskhimizdat, Moscow, 1962.
11. B.G.Eremina, "Gazovyi Analiz" (Gas Analysis), Goskhimizdat, Moscow–Leningrad, 1955, p.115.
12. F.D.Rossini, D.D.Wagman, W.H.Evans, S.Levine, and I.Jaffe, "Selected Values of Chemical Thermodynamic Properties", U.S.Nat.Bur.Standards, Circ.500, U.S.Govt. Printing Office, Washington, 1952.
13. G.Humphrey and E.King, J.Amer.Chem.Soc., 74, 204 (1962).

Received 9th August 1963

U.D.C. 543.1

# THE FORMULATION OF BOGOLYUBOV'S EQUATIONS FOR UNARY FUNCTIONS IN THE STATISTICAL THEORY OF THE ELECTRICAL DOUBLE LAYER

R.R.Dogonadze and Yu.A.Chizmadzhev

In the formulation of equations of the statistical theory of the electrical double layer difficulties of two kinds arise. The first of these is of strictly statistical origin. Equations of correlative functions have been formulated[1] for a system of particles in an external field. In setting up a theory of the electrical double layer, it is necessary to consider a system of charged particles in the vicinity of a metal plane, but since it is impossible to disregard the effect of the particles on charge distribution in the metal, the influence of the metal does not reduce to the usual external field.

In addition, there are difficulties in the formulation of the electrostatic problem for a system of charged particles in a "half-space" in the presence of only one metal plane. It will be shown below that two metal planes (electrodes) at a distance $L$ must be considered simultaneously. After formulation of the statistical problem, $L$ may be taken to the limit $L \to \infty$.

## Distribution Function for Charged Particles Between Two Metal Planes

Consider a system consisting of ions in solution, solvent, free electrons, and ionic residues of metal electrodes. The surrounding medium and the battery, with which charge exchange takes place if the potentials of the plates are fixed, function as a thermostat. It is also possible to consider the problem with electrodes on open circuit, bearing a fixed charge. The difference between these two problems is that in the first case the chemical potentials of electrons ($\mu_e$) and in the second their number ($N_e$) are specified.

Consider the potentiostatic case. The distribution function for the system as a whole is

$$dw_{iM} = A \exp\{-\beta[E_i + E_M + V_{iM} - \bar{\mu}_1 N_1^e - \bar{\mu}_2 N_2^e]\}\, dR_i dM, \qquad (1)$$

where $E_i$ is the energy of ions in solution, $E_M$ the energy of the metal and solvent, $V_{iM}$ the energy of interaction between them, $\bar{\mu}_1$ and $\bar{\mu}_2$ are the electrochemical potentials of electrons in electrodes 1 and 2, $N_1^e$ and $N_2^e$ represent the numbers of electrons in the two electrodes, $R_i$ are the coordinates of the ions, and $M$ the coordinates of all the remaining components of the system. On integrating

Eqn. (1) with respect to $M$, we obtain the distribution function for the ions:

$$dw_i = A \sum_{N^e_{1,2}} dR_i \int \exp\{-\rho[E_i + E_M + V_{iM} - \bar{\mu}_1 N_1^e - \bar{\mu}_2 N_2^e]\}\, dM = A' e^{-\beta E_i} Z_M(R_i)\, dR_i. \quad (2)$$

Here $Z_M(R_i)$ is the partition function of the system, excluding ions, which depends on the ionic coordinates $R_i$. Using the relation

$$F_M - \bar{\mu}_1 N_1^e - \bar{\mu}_2 N_2^e = -kT \ln Z_M,$$

we obtain

$$dw_i = A' e^{-\beta[E_i + E_M - \bar{\mu}_1 \bar{N}_1^e - \bar{\mu}_2 \bar{N}_2^e]} dR_i.$$

Here $F_M = F^0_M + F_{M,\,elst}$, where only $F_{M,\,elst}$ (the electrostatic part of the free energy) and $\bar{N}_1^e$ and $\bar{N}_2^e$ depend on $R_i$. Subsequently, all terms which do not depend on $R_i$ will be omitted from normalisation expressions.

Since $E_i$ contains only the electrostatic part of the energy (for simplicity, short-range interactions are not considered), it is identical with $F_i$:

$$dw_i \simeq \exp\{-\beta[F_M(R_i) + F_i(R_i) - \bar{\mu}_1 N_1^e - \bar{\mu}_2 N_2^e]\} dR_i. \quad (3)$$

Eqn. (3) shows that in this case the free energy of the system for fixed $R_i$ plays the role of the potential energy. This constitutes the difference between the present system and the usual problems with an external field.

Instead of $\bar{N}^e_{1,2} = \bar{N}^e_1$ and $\bar{N}^e_2$, it is convenient to introduce the charges $\bar{q}_{1,2} = \bar{q}_1$ and $\bar{q}_2$ by means of the formula

$$q_{1,2} = e[\bar{N}^i_{1,2} - \bar{N}^e_{1,2}],$$

where $\bar{N}^i_{1,2}$ represent the number of ionic residues of the two electrodes, *i.e.*

$$\bar{N}^e_{1,2} = \bar{N}^i_{1,2} - q_{1,2}/e.$$

The calculation of the exponent in Eqn. (3) is begun with the last terms:

$$\mu_1 N_1^e + \mu_2 N_2^e = \bar{\mu}_0(N_1^i + N_2^i) - e\varphi_1 N_1^i - e\varphi_2 N_2^i + \mu_0/e\,(q_1 + q_2) + \varphi_1 q_1 + \varphi_2 q_2.$$

The first three terms must be omitted, since they do not depend on $R_i$. In the solution of the electrostatic problem it will be shown that $q_1 + q_2 = 0$, so that

$$dw_i \simeq \exp\{-\beta[F(R_i) - q_i\varphi_M]\} dR_i, \quad (4)$$

where $\varphi_M = \varphi_1 - \varphi_2$.

## Calculation of $U_N$

Initially we shall calculate $F(R_i)$ for the case in which the potential is fixed. Consider an electrically neutral system of charged particles between two metal electrodes; a specified potential difference $\varphi_1 - \varphi_2 = \varphi_M$ is maintained between the electrodes. It is known that[2]

$$F = \frac{1}{2} q_1 \varphi_M + \frac{1}{2} \sum_1^N e_i \tilde{\varphi}(R_i;\, R_{1,\ldots,N}), \quad (5)$$

where $\tilde{\varphi}(R_i;\ R_{1,\ldots,N})$ is the potential at $R_i$ due to the electrodes and all the ions except the $i$-th ion.

The potential $\varphi(r;\ R_k)$ at any point is defined by the Poisson equation

$$\Delta_r \varphi = -\frac{4\pi}{\varepsilon} \sum e_i \delta(r - R_i) \quad (6)$$

with the boundary conditions $\varphi(x = 0) = \varphi_1$ and $\varphi(x = L) = \varphi_2$. The electrodes will be assumed to have an infinite area, so that

$$\varphi = \varphi_0 + \varphi_1 + \frac{\varphi_2 - \varphi_1}{L} x,$$

where $\varphi_0$ is the solution of Eqn. (6) for zero boundary conditions. Then

$$\tilde{\varphi}_i = \lim_{r \to R_i} [\varphi - e_i/|r - R_i|] = \tilde{\varphi}_0 + \varphi_1 + \frac{\varphi_2 - \varphi_1}{L} x. \quad (7)$$

The charge on the electrodes is

$$q_1 = -\frac{\varepsilon}{4\pi} \int \frac{\partial \varphi}{\partial x}\Big|_1 ds = \frac{\varepsilon S}{4\pi L} \varphi_M + q_1^0.$$

Using the expression for $\varphi_0$ obtained by Krylov[3], it can be readily shown that

$$q_1^0 = \sum_i (-e_i) \frac{L - x_i}{L} = \frac{1}{L} \sum e_i x_i$$

$$q_2^0 = -\frac{1}{L} \sum e_i x_i.$$

Then

$$\left.\begin{aligned} q_1 &= \frac{\varepsilon S}{4\pi L} \varphi_M + \frac{1}{L} \sum e_i x_i \\ q_2 &= -\frac{\varepsilon S}{4\pi L} \varphi_M - \frac{1}{L} \sum e_i x_i \end{aligned}\right\}, \quad (8)$$

*i.e.*

$$q_2 + q_1 = 0.$$

Omitting the constant terms, we obtain

$$U_N = F - q_1 \varphi_M \simeq \frac{1}{2} \sum_{i=1}^N e_i \tilde{\varphi}_0^i - 4\pi\sigma_0 \sum e_i x_i, \quad (9)$$

where $\sigma_0 = \varphi_M / 4\pi L$ is the charge density which would have arisen on the electrodes in the absence of electrolyte. It is more convenient to represent the energy $U_N$ by a sum of interactions in pairs:

$$\varphi_0 = \sum_i \psi_i(r,\, R_i),$$

where $\psi_i$ is the potential due to the $i$-th ion at point $r$ under zero boundary conditions. Then

$$\tilde{\varphi}_0^i = \sum_{k \neq i} \psi_k(R_i;\ R_k) + \psi_i(x_i),$$

where $\psi_i(x_i)$ is the potential at point $x_i$ due to the images of the $i$-th ion. Eqn. (9) can be rewritten in terms of $\psi_i$ as follows:

$$U_N \simeq \frac{1}{2} \sum\sum_{i \neq k} e_i e_k \psi(R_i;\ R_k) + \frac{1}{2} \sum_i e_i^2 \psi(r_i) - 4\pi\sigma_0 \sum e_i x_i. \quad (10)$$

Here $\psi$ denotes the potential due to a single positive charge. It may be shown that in the case where the total charge on the electrodes is fixed, the energy $U_N$ becomes

$$U_N = \frac{1}{2} \sum e_i \varphi_i^0 - \frac{1}{L} \sum e_i x_i \left[\frac{4\pi\sigma L}{\varepsilon} - \frac{2\pi}{\varepsilon S} \sum e_k x_k\right]. \quad (11)$$

## Formulation of the Equations and Boundary Conditions for Correlative Functions

The case of fixed potential. Usually Bogolyubov's equations are used in the limiting form ($N \to \infty$, $V \to \infty$, $N/V$ = const). However, in our problem, with a finite $L$, it is possible to carry out only the following

limiting transformations: $S \to \infty$, $N \to \infty$, $N/V$ = const. In the case of a specified potential the equation for a unary function is

$$\frac{\partial K_1}{\partial x_1} - \frac{\beta e_1 \varphi_M}{L} K_1 + \frac{\beta e_1}{2} \frac{d\psi_1^0}{dx_1} K_1 + \beta e_1 \sum_c \nu_c \int \left[ \frac{\partial \psi_{1c}^0 (R_c R_1)}{dx_1} \right] K_{c1} dR_c = 0. \quad (12)$$

It follows from the derivation of Eqn. (12) that the only additional condition is the normalisation condition for the correlative function. Going to the limit $L \to \infty$ directly in Eqn. (12) is incorrect if only because the only term which depends on the field disappears and the boundary conditions at infinity are independent of the field. It may be shown that, in taking Eqn. (12) to the limit $L \to \infty$, it is necessary to specify yet another boundary condition† [apart from the usual condition for the weakening of correlation $K(\infty) = 1$], which depends on $\varphi_M$. To illustrate this we shall examine Eqn. (12), using the zeroth approximation for the Debye parameter‡:

$$r_0 / r_d = 0.$$

It is known that in this case the equation reduces to an integral form:

$$-u_1(x_1) + A_1 - \frac{e_1 \varphi_M}{L} x_1 + e_1 \int \psi^0 (R, R_1) \rho(x) dR = 0, \quad (13)$$

where $u_1(x_1) = -1/\beta \ln K_1(x)$ and $\rho = e\nu(K_+ - K_-)$. Putting $x_1 = L/2$, we find $A_1 = u_1(L/2) + e_1\varphi_M/2$. On substituting $A_1$ in Eqn. (13) and putting $x_1 = 0$, we obtain

$$-u_1(0) + u_1(L/2) + \frac{e_1 \varphi_M}{2} = 0.$$

It follows from the condition for the weakening of correlation that $u_1(L/2) \to 0$ when $L \to \infty$. Consequently $u_1(0) = e_1\varphi_M/2$ when $L \to \infty$. For $u < kT$, the integrodifferential equation corresponding to Eqn. (13) (when $L \to \infty$) is

$$\frac{\partial u_+}{\partial x_1} + 2e^2\nu\beta \int \frac{\partial}{\partial x_1} \psi^0 u_+ dR = 0. \quad (14)$$

This equation is homogeneous, *i.e.* $u$ is defined to within an arbitrary multiplier, and at infinity $u \to 0$. Consequently the condition $u(\infty) = 0$ does not define the solution. We may note that the initial equation (13) was inhomogeneous and defined a unique solution satisfying the condition $u(0) = e\varphi_M/2$. Hence the required solution may be found by imposing, for example, the condition $u(0) = e\varphi_M/2$. We thus conclude that Eqn. (14) must be given another boundary condition at zero.

Hitherto in discussions of the statistical theory of the double layer the following equation[3,4] has been used:

$$\frac{\partial u_1}{\partial x_1} + 4\pi\sigma e + \frac{\varkappa^2}{4\pi} \int \frac{\partial \psi^0}{\partial x_1} u_1 dR = 0, \quad (15)$$

where $\sigma$ is understood to be the average density of the overall charge on the electrode. It is seen from Eqn. (12) that in actual fact instead of $\sigma$ the equation contains $\sigma_0 = \varphi_M/4\pi L$, which tends to zero when $L \to \infty$.

It can be readily shown that for finite $L$ the solution of Eqn. (13) is

$$u_1 = \frac{e_1 \varphi_M}{2(1 - e^{\varkappa L})} [e^{\varkappa x} - e^{\varkappa(L-x)}]. \quad (16)$$

When $L \to \infty$, this expression can be written thus:

$$u_1 = \frac{e_1 \varphi_M}{2} e^{-\varkappa x}. \quad (17)$$

† As will be shown below, for the limit $L \to \infty$ it is also necessary to transform the integrand in Eqn. (12).

‡ As usual, $r_0 = e^2/kT$ and $r_d = 1/\varkappa$.

It can be easily demonstrated that this well-known solution for a unary function satisfies the integrodifferential Eqn. (15) with $\sigma = 0$.

Actually, in examining an unbounded system it is not necessary to solve the problem with a finite $L$, taking the limit $L \to \infty$ only in the final expression for $u$; the limiting transformation may be carried out directly in Eqn. (12), which includes terms for the double layer at both electrodes. In order to "break the connection" between the double layers, we writen the integral term of Eqn. (17)§ as follows:

$$\int_0^L \psi^0 \rho(x) dR = \int_0^{L/2} \ldots + \int_{L/2}^L \ldots$$

After integration with respect to $y$ and $z$, we obtain for the second integral

$$\int_{L/2}^L \ldots = \int_{L/2}^L \left[ \frac{x_1 + x}{2} - \frac{x_1 x}{L} - \frac{|x_1 - x|}{2} \right] u(x) dx.$$

When the change of variables $x = L - x'$ is carried out,

$$\int_{L/2}^L \ldots = \int_0^{L/2} - \frac{x_1 x'}{L} u(x') dx', \quad x_1 < L/2.$$

Combining the result with the first integral, we have

$$\int_0^L \ldots = \int_0^{L/2} \left[ \frac{x_1 + x}{2} - \frac{|x_1 - x|}{2} - \frac{x_1 x}{L/2} \right] u(x) dx. \quad (18)$$

We have thus "broken the connection" between the double layers, since the integral is taken from 0 to $L/2$. It is now possible to go to the limit $L \to \infty$ in the integrand since $\int_0^{L/2} xu(x)dx$ is finite. The last term in Eqn. (18) then becomes zero. The resulting expression after this limiting transformation has function (17) as a solution, *i.e.* it describes a single double layer. Hence in solving the problem with one boundary at infinity (the "semi-infinite" problem), it is necessary to set $\sigma_0$ equal to zero in Eqn. (12), modify the integration limits so that one of them is at infinity, and identify $\psi^0$ with the Green function for the electrostatic problem with charge $y$ on a single metal plate.

When $L$ is small, the average charge on the metal is not equal to the charge of the double layer in solution. Indeed, it can be readily shown that, when $e\varphi/kT \ll 1$, their difference is

$$|\sigma_M| - |\sigma_d|| = -\frac{4\pi}{\varepsilon} \varphi'(L/2) = \frac{2\pi\varphi_M \varkappa}{\varepsilon \sinh \varkappa L/2}, \quad (19)$$

$$\sigma_M = \frac{\varepsilon}{8\pi} \varphi_M \varkappa \tanh L/2 \to \frac{e\varphi_M \varkappa}{8\pi} \text{ when } L \to \infty. \quad (20)$$

The case of a fixed charge. On substituting the expression for the energy from Eqn. (11) in the zeroth approximation for a unary function, we obtain

$$\frac{d \ln K_1}{dx} - \frac{4\pi\sigma e_1 \beta}{\varepsilon} + \frac{4\pi\beta e_1}{\varepsilon L} \sum_c e_c \nu_c \int_0^L x K_c(x) dx + \beta e_1 \sum e_c \nu_c \int \frac{\partial \psi^0 (R_1, R)}{\partial x_1} K_c(x) dR = 0. \quad (21)$$

This equation differs from Eqn. (12) by the presence of a third term and the fact that Eqn. (21) includes the overall charge density $\sigma = q/S$ instead of $\sigma_0$ as in Eqn. (12). However, in actual fact Eqns. (21) and (12) are completely

§ For clarity we shall confine ourselves to the case $r_0/r_d \ll 1$.

analogous, which can be demonstrated by calculating $\overline{\varphi}_M$. On averaging $\varphi_M$, we obtain

$$\frac{\beta e_1 \overline{\varphi}_M}{L} = \frac{4\pi\sigma e_1 \beta}{\varepsilon} - \frac{4\pi e_1 \beta}{\varepsilon L} \sum_c \nu_c e_c \int_0^L x K_c(x)\, dx. \qquad (22)$$

Hence Eqn. (21) may be rewritten as follows:

$$\frac{d \ln K_1}{dx_1} - \frac{\beta e_1 \overline{\varphi}_M}{L} + \beta e_1 \sum e_c \nu_c \int \frac{\partial \psi^0}{\partial x_1} K_c(x)\, dR = 0. \qquad (23)$$

Eqn. (23) is now identical with Eqn. (12), but includes $\overline{\varphi}_M$ instead of $\varphi_M$ as in Eqn. (12). It is therefore possible to use Eqn. (16) to establish the relation between $\overline{\varphi}_M$ and $\sigma$:

$$\overline{\varphi}_M = \frac{8\pi\sigma \tanh \varkappa L/2}{\varepsilon \varkappa} \simeq \frac{8\pi\sigma}{\varepsilon \varkappa}. \qquad (24)$$

Hence $\overline{\varphi}_M$ remains finite when $L \to \infty$ and the limiting transformation $L \to \infty$ can be carried out in Eqn. (23) as before, specifying an appropriate additional boundary condition for the equation.

In conclusion, it should be noted that the problem with a specified $\sigma$ is completely equivalent to the problem with a specified $\varphi_M$, which was discussed in detail above. This can be shown by means of the exact equation for a unary function.

The authors thank V. G. Levich for discussing the results of the present investigation.

## SUMMARY

1. A distribution function has been obtained for a system of charged particles between two planar electrodes at a distance $L$. The effective potential energy of this system has been found. The cases of a specified potential and a specified charge have been considered.

2. Equations have been formulated for unary correlative functions with finite $L$. A study has been made of the limiting transformation $L \to \infty$. The cases of a specified potential and a specified charge have again been considered.

1. N. N. Bogolyubov, "Problemy Dinamicheskoi Teorii v Statisticheskoi Fizike" (Problems of Dynamic Theory in Statistical Physics), Gostekhizdat, Moscow–Leningrad, 1946.
2. L. D. Landau and E. M. Lifshits, "Elektrodinamika Sploshnykh Sred" (Electrodynamics of Continuous Media), Fizmatgiz, 1960.
3. V. S. Krylov, Thesis, Institute of Electrochemistry of the USSR Academy of Sciences, 1963.
4. V. A. Kir'yanov, Thesis, MIFI, 1958.

Institute of Electrochemistry, USSR Academy of Sciences

Received 17th August 1963

U. D. C. 532.7

# MISCIBILITY IN THE ISOPROPANOL–BENZENE–WATER SYSTEM

V. V. Udovenko and T. F. Mazanko

In our previous papers data on the miscibility in methanol–benzene–water[1] and n-propanol–benzene–water[2] systems were given. The present paper deals with the miscibility in the ternary system isopropanol–benzene–water. The miscibility was measured by Alekseev's method[3] in the temperature range 20–70°. Isopropanol had the following physical constants: b.p. 81.4° ($p$ = = 750 mmHg); $d_4^{30}$ = 0.7971; $n_D^{25}$ = 1.3749; the physical constants of benzene were the same as before[2].

## EXPERIMENTAL

Five property–temperature curves were obtained with a constant alcohol : benzene ratio and four with a constant alcohol : water ratio. The results of the measurements are presented in Table 1. Miscibility isotherms for 30°, 45°, and 60° were plotted on the basis of the data obtained. In this system, as in those with methanol and n-propanol, there is a single heterogeneous region (two liquid layers) adjacent to the water–benzene side of the triangular diagram.

Miscibility in the isopropanol–benzene–water system has been studied at 25° by Olsen and Washburn[4]. According to our data, at 25° the miscibility along the section of the isotherm adjacent to the isopropanol–benzene side of

TABLE 1. Miscibility in the isopropanol–benzene–water system.

| Benzene, wt. % | t, °C | Water, wt. % | t, °C |
|---|---|---|---|
| Alcohol : water = 16.50 : 83.50 | | Alcohol : benzene = 15.30 : 84.70 | |
| 0.182 | 18.92 | 1.255 | 22.00 |
| 0.266 | 25.18 | 1.397 | 34.20 |
| 0.412 | 35.88 | 1.505 | 48.18 |
| 0.510 | 45.15 | 1.609 | 57.35 |
| 0.643 | 56.00 | 1.674 | 68.78 |
| 0.738 | 64.72 | Alcohol : benzene = 27.59 : 72.41 | |
| Alcohol : water = 29.51 : 70.49 | | 3.61 | 19.72 |
| 1.31 | 19.80 | 3.73 | 30.70 |
| 1.79 | 28.85 | 3.83 | 41.50 |
| 2.28 | 39.86 | 3.96 | 50.45 |
| 2.85 | 51.66 | 4.19 | 65.37 |
| 3.73 | 69.39 | Alcohol : benzene = 45.70 : 54.30 | |
| Alcohol : water = 45.79 : 54.21 | | 9.96 | 19.90 |
| 8.29 | 21.95 | 10.27 | 35.10 |
| 8.80 | 27.98 | 10.39 | 42.90 |
| 9.79 | 41.00 | 10.62 | 50.88 |
| 10.23 | 51.12 | 10.87 | 60.41 |
| 10.81 | 57.51 | Alcohol : benzene = 60.18 : 39.82 | |
| 11.26 | 66.70 | 18.70 | 19.20 |
| Alcohol : water = 59.50 : 40.50 | | 18.98 | 28.25 |
| 18.31 | 20.81 | 19.46 | 43.75 |
| 18.76 | 30.83 | 19.86 | 54.51 |
| 19.28 | 46.39 | 20.33 | 64.75 |
| 19.86 | 62.42 | Alcohol : benzene = 74.50 : 25.50 | |
| 20.30 | 68.55 | 36.70 | 19.01 |
| | | 37.52 | 28.25 |
| | | 38.10 | 31.93 |
| | | 38.99 | 41.49 |
| | | 39.95 | 49.80 |
| | | 40.97 | 63.60 |