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The Water/Oil/Water Thermocouple and the Ionic Seebeck Effect

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A new type of non-isothermal galvanic cell comprising two interfaces between immiscible electrolyte solutions is presented. It is shown that if only one ion can partition across the liquid/liquid interface, the water/nitrobenzene/water cell behaves as a performant thermocouple. The thermodynamic treatment shows that the thermopower of this system is equal to the difference of transported entropies of the partitioning ion.

In 1821 Seebeck¹ observed that heating one junction of a bimetallic couple and cooling the other gave rise to an electromotive force in the circuit as illustrated in fig. 1. These observations were followed in 1834 by those of Peltier,² who reported that the passage of an electric current through the same bimetallic circuit causes absorption of heat at one junction and liberation of heat at the other. In 1854 William Thomson (Lord Kelvin)³ analysed the energy balance of these thermoelectric phenomena and showed that the thermoelectric e.m.f., E , is related to the so called ‘Peltier heat’, Π , and the ‘Thomson heat’, θ , by

$$\frac{dE}{dT} = \frac{d(\Pi_A - \Pi_B)}{dT} + (\theta_A - \theta_B) \quad (1)$$

where T denotes the absolute temperature.

However, the full rationalization of the Thomson equation of thermoelectricity came only this century with the development of the thermodynamics of irreversible processes.⁴ By introducing the concept of transported entropy of a species, i , $*S_i$, defined as the entropy transported through a reference plane at vanishing temperature gradients it can be shown that the thermoelectric power, ε_{AB} , of a thermocouple is related to the difference between the transported entropies of the electrons in the two conductors A and B:⁵

$$\varepsilon_{AB} = \frac{dE}{dT} = \frac{1}{F} [(*S_{e^-})_A - (*S_{e^-})_B]. \quad (2)$$

In a similar manner, the Thomson and the Peltier ‘heats’ can be expressed, respectively, as

$$\theta = \frac{-T}{F} \left(\frac{\partial *S_{e^-}}{\partial T} \right)_p \quad (3)$$

and

$$\pi = \frac{T}{F} *S_{e^-}. \quad (4)$$

The transported entropy plays a central role in non-isothermal transport processes not only in electron conductors but also in electrolyte solutions. As thoroughly reviewed by Agar,⁶ the transported entropy of individual ionic species can be evaluated from the

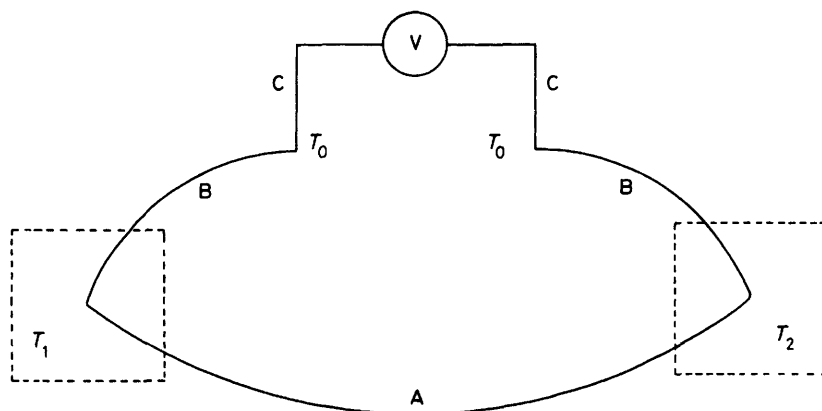
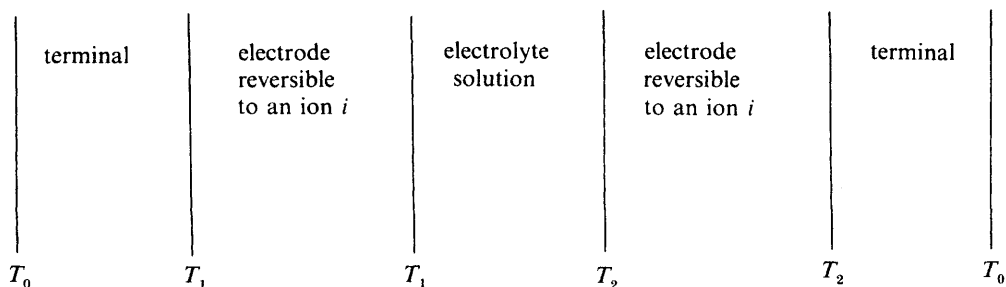


Fig. 1. Thermocouple of the conductors A and B. The voltmeter and the junctions A/C and B/C are kept at room temperature while the two junctions A/B and B/A are kept at T_1 and T_2 , respectively.

measurement of the thermopower of thermogalvanic cells as generally represented by the diagram:



For such a system the steady-state thermopower can be expressed by

$$\epsilon_{st} = \frac{-1}{F} \left(\frac{*S_i}{z_i} + *S_e - \frac{S_a}{z_i} \right) \quad (5)$$

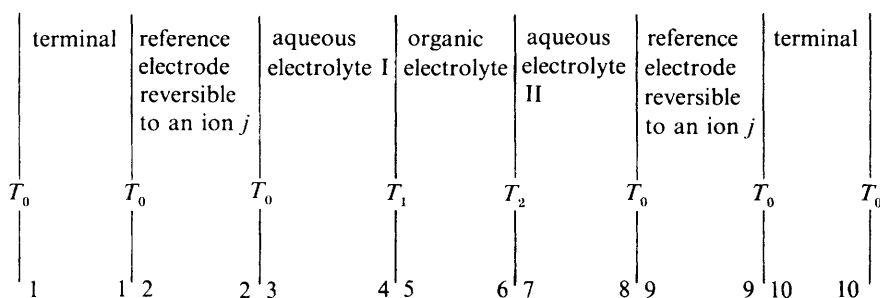
where S_a denotes a certain linear combination of the partial molar entropies of substances in the electrodes (*e.g.* for silver/silver chloride electrodes: $S_a = S_{AgCl} - S_{Ag}$). Therefore, by normalizing the last two terms of eqn (5), the transported entropy of the species can be obtained from the measurement of the e.m.f. of the thermocells.

In the case of non-aqueous electrolytes, the number of reference electrodes is rather restricted, and very few data are available. The purpose of the present communication is to show that, however, in the case of organic solvents which are immiscible with water, it is possible to build a water/oil/water thermocouple to measure the difference of transported entropies of any species partitioned between the two phases. As recently reviewed,⁷ electrochemical studies of the interface between two immiscible electrolyte solution (ITIES) have permitted the elaboration of a rather well defined model of the interface. Surface tension⁸ and capacitance measurements⁹ have shown in particular that unlike the electrode/electrolyte interface there is no inner layer of oriented solvent molecules, and the interface can in fact be regarded as a mixed solvent layer no more

than 3 nm thick. Despite the relatively good level of understanding of the interfacial structure, the degree of comprehension of charge-transfer phenomena across an ITIES is, however, rather limited. In particular, in the case of ion-transfer reactions no satisfactory mechanism has yet been proposed. The real question is to know if ion-transfer reactions are activated processes, and if so how much do they differ from ionic transport processes in electrolyte solution. In the same way that the measurements of partial molar entropy of ions in solution have contributed to the present knowledge of ion-solvent interactions by forwarding the concept of structure making/breaking effect,¹⁰ it is expected that the measurements of transported entropy of ion, and the subsequent evaluation of the corresponding heat of transport (*vide infra*) should shine new lights on ion-transfer reactions across an ITIES.

The Water/Oil/Water Thermocouple

Schematically, a water/oil/water thermocouple can be represented by the following cell:



It is assumed that the two ITIES formed are reversible to an ion i only. In this case the system behaves as an ideal liquid-membrane ion-selective electrode for the ion i .

The measured e.m.f., E , is taken as the difference between the electric potential in the right-hand terminal and that in the left-hand terminal, measured with no current flowing ($E = \Phi_{10} - \Phi_1$). Because the two electrode/terminal junctions are at the same temperature T_0 , the differences $(\Phi_{10} - \Phi_9)$ and $(\Phi_2 - \Phi_1)$ cancel out. So do the differences $(\Phi_9 - \Phi_8)$ and $(\Phi_3 - \Phi_2)$ if we assume that in the vicinity of the electrodes the activity of the ion j remains unchanged. This assumption can be satisfied experimentally by interposing between the ITIES and the reference electrode an electrolyte sealed tap to ensure that the breakdown of the molarity homogeneity by the Soret effect occurs mainly between the tap and the ITIES (see fig. 2).

The differences $(\Phi_8 - \Phi_7)$, $(\Phi_6 - \Phi_5)$ and $(\Phi_4 - \Phi_3)$ are thermal diffusion potentials given by

$$F \text{ grad } \Phi = - \sum_k \tau_k \left((\text{grad } \mu_k)_{T,p} + \frac{*Q_k}{T} \text{ grad } T \right) \quad (6)$$

where k stands for the different ionic species in solution, τ is the reduced transport number ($\tau = t/z$) and μ is the chemical potential. $(\text{grad } \mu_k)_{T,p}$ signifies the gradient of chemical potential at constant temperature and pressure, and refers therefore only to the change of chemical potential with concentration. At stationary state, the flux of the species i , which is the only species crossing the ITIES, is equal to zero in the three electrolyte solutions.

In this case, eqn (6) reduces to

$$z_i F \text{ grad } \Phi = - (\text{grad } \mu_i)_{T,p} - \frac{*Q_i}{T} \text{ grad } T \quad (7)$$

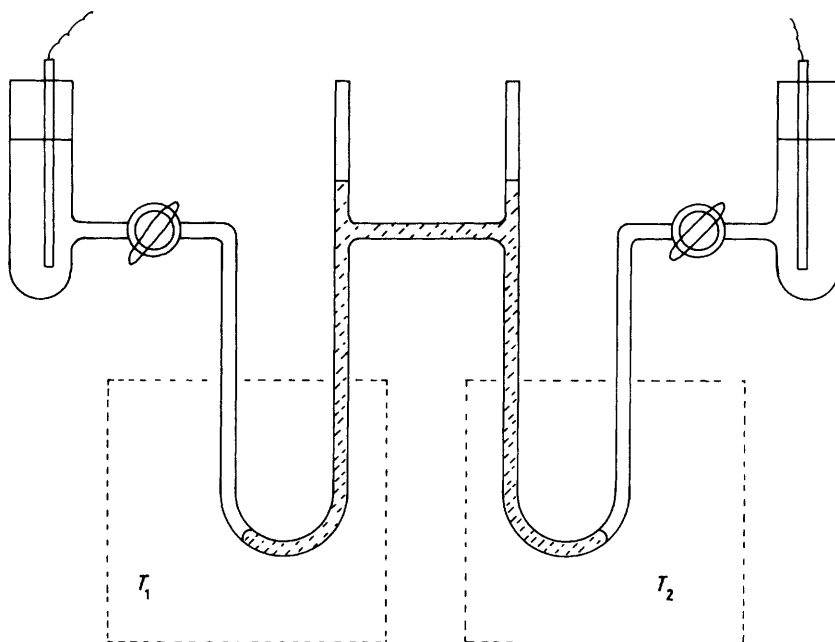


Fig. 2. Water/nitrobenzene/water thermocouple with Ag/AgCl reference electrodes.

where *Q_i represents the heat transported by the ion i through a fixed reference plane in the Hittorf system at vanishing temperature gradient. This quantity, often called⁵ the heat of transport, is related to the transported entropy, *S_i , by

$${}^*Q_i = T({}^*S_i - S_i) \quad (8)$$

where S_i denotes the partial molar entropy. As clearly summarized by Haase,⁵ a Hittorf reference system is defined by assuming the reference velocity is the average velocity of all solvent molecules, including solvation molecules. In this case the total flux of the solvent across a reference plane is equal to zero. By substituting eqn (8) into eqn (7), we then obtain the thermal diffusion potential in the oil phase:

$$z_i F(\Phi_6 - \Phi_8) = -\Delta_I^{\text{II}}(\mu_i^o)_{T,p} - \int_{T_2}^{T_1} ({}^*S_i^o - S_i^o) dT \quad (9)$$

where the subscript (o) refers to the organic phase. Similarly, the sum of the thermal diffusion potential in the two aqueous phases is then equal to

$$z_i F[(\Phi_8 - \Phi_7) + (\Phi_4 - \Phi_3)] = \Delta_I^{\text{II}}(\mu_i^a)_{T,p} + \int_{T_1}^{T_2} ({}^*S_i^a - S_i^a) dT. \quad (10)$$

The differences $(\Phi_7 - \Phi_6)$ and $(\Phi_5 - \Phi_4)$ represent the two potential drops across the two ITIES. By assuming that the ion i is the only potential-determining ion across the ITIES, these potential differences can be obtained from the equality of the electrochemical potential of the ion between the two phases:

$$\tilde{\mu}_i^a = \tilde{\mu}_i^o \quad (11)$$

to give

$$\begin{aligned} z_i F[(\Phi_7 - \Phi_6) + (\Phi_5 - \Phi_4)] &= [(\mu_i^o)_{\text{II}} - (\mu_i^a)_{\text{II}}] + [(\mu_i^a)_1 - (\mu_i^o)_1] \\ &= \Delta_I^{\text{II}}(\mu_i^o) - \Delta_I^{\text{II}}(\mu_i^a). \end{aligned} \quad (12)$$

If we consider the system to be in mechanical equilibrium ($\text{grad } p = 0$), the chemical potential gradient can be written as

$$\text{grad } \mu_i = -S_i \text{ grad } T + (\text{grad } \mu_i)_{T,p} \quad (13)$$

and eqn (12) therefore can be rewritten as

$$z_i F [\Delta_6^2 \Phi + \Delta_4^5 \Phi] = \Delta_I^{\text{II}}(\mu_i^o)_{T,p} - \Delta_I^{\text{II}}(\mu_i^a)_{T,p} - \int_{T_1}^{T_2} S_i^o dT + \int_{T_1}^{T_2} S_i^a dT. \quad (14)$$

If the compositions of the two aqueous electrolytes I and II are identical, then by combining eqn (9), (10) and (14), the total potential difference across the cell is given by

$$z_i F E = \int_{T_1}^{T_2} (*S_i^a - *S_i^o) dT. \quad (15)$$

It can therefore be concluded that the thermopower of a water/oil/water thermocouple can be expressed as

$$\varepsilon = \frac{dE}{dT} = \frac{*S_i^a - *S_i^o}{z_i F}. \quad (16)$$

The analogy between eqn (1) and (16) shows that the Seebeck effect observed so far for electron conductors can also be observed for ionic conductors in systems such as the one described above. Pursuing the analogy further allows the definition of ionic Thomson and Peltier 'heats' as

$$\theta = \frac{T}{z_i F} \left(\frac{\partial *S_i}{\partial T} \right)_p \quad (17)$$

and

$$\Pi = \frac{-T}{z_i F} *S_i. \quad (18)$$

Experimental

The aqueous electrolyte was a solution of 0.1 mol dm^{-3} NaCl and 0.01 mol dm^{-3} tetrabutylammonium chloride, TBACl, in doubly deionized water. The organic electrolyte was a 0.01 mol dm^{-3} solution of tetrabutylammonium tetraphenylborate, TBATPB, in nitrobenzene. TBATPB was prepared by mixing equimolar aqueous solutions of TBACl and NaTPB. The precipitate obtained was dried and recrystallized twice from AnalaR acetone (BDH). Nitrobenzene (Fisons, SLR) was used without purification. The two immiscible electrolyte solutions were equilibrated in a separating funnel for a day prior to the experiment.

The cell used is composed of two U-tubes as shown in fig. 2. Two water baths thermostatted by thermostirrers having an accuracy of 0.1°C were used for the non-isothermal measurements. One bath (I) was kept at constant temperature $T_1 = 19.7^\circ \text{C}$ while the temperature of the second bath was varied. The temperatures of the baths were monitored by NiCr/NiAl Comark 2001 digital thermometers. The room temperature was $20 \pm 2^\circ \text{C}$.

Silver/silver chloride rod electrodes were used as reference electrodes. The two electrodes were checked before and after the experiment in KCl solution. The e.m.f. of the thermocell was measured with a battery-operated electrometer (Keithley 602). Because of the relatively high impedance of the cell used (a few megohms) and the absence of a noise-protection system such as a Faraday cage, the accuracy of the measurement was not better than 0.2 mV .

At the beginning of the measurement the cell was placed in bath I, of which the temperature was near that of the room, and the equilibrium e.m.f., E° , was recorded. The non-isothermal e.m.f. was measured by placing one of the U-tubes in the second bath. The steady-state response was reached well within a minute. The cell was then replaced in bath I and the equilibrium value was reached again also within a minute. For a given temperature, T_i , five measurements were taken. Between each series of measurements, the cell was left standing at room temperature. The relative speed for the establishment of a steady-state value tends to show that the effect observed is not due to the variation of the mutual solvent solubility with temperature. Such an effect is likely to cause a drift of the steady-state value over a longer timescale and should not impede the present observation.

Results and Discussion

The interface between an aqueous solution of tetrabutylammonium chloride (TBACl) and a solution of tetrabutylammonium tetraphenylborate (TBATPB) in nitrobenzene has been well characterized. Gavach has shown¹¹ that in this case the Galvani potential difference between the two phases is solely determined by the concentration of TBA^+ in the two phases. Indeed, the solubilities of NaCl in nitrobenzene and TBATPB in water are so low that the only ion able to partition will be TBA^+ if some TBACl is added to the aqueous phase. The free exchange of this ion between the two phases makes it the only potential determining ion. Therefore, in the system chosen, eqn (12) is fully verified.

Table 1 gives the results obtained with the cell described above in the order of data acquisition, and fig. 3 illustrates the e.m.f. of the water/nitrobenzene/water thermocouple reversible to tetrabutylammonium.

The slope at the origin, which represents the thermopower of the thermocouple, is *ca.* -1.25 mV K^{-1} . The results show that, at 20°C , the difference of transported entropies of tetrabutylammonium ion between water and nitrobenzene is equal to

$$*S_{TBA^+}^{NB} - *S_{TBA^+}^{H_2O} = 120 \text{ J K}^{-1}.$$

The corresponding Peltier heat difference is therefore equal to

$$\Pi_{TBA^+}^{NB} - \Pi_{TBA^+}^{H_2O} = 0.37 \text{ J}.$$

These results show that the water/nitrobenzene/water thermocouple reversible to TBA^+ forms a very performant thermocouple. Bimetallic devices made from pure metals have a thermopower which can only reach a few hundred $\mu\text{V K}^{-1}$. Only thermocouples made from metallic alloys can provide a thermopower as high as 1 mV K^{-1} . As discussed below, the high performance of ionic systems can be attributed to the relatively high entropy of transfer of the partitioning ion (*e.g.* TBA^+) between immiscible liquids compared with the entropy of transfer of the electrons between two metals. According to eqn (8), the difference of transported entropy between the two phases is equal to the sum of the entropy of transfer, ΔS , and the difference of Eastman entropy, $*Q/T$:

$$\Delta *S = \Delta S + (\Delta *Q/T). \quad (19)$$

The entropy of transfer is classically defined as the difference of partial molar entropy and can be expressed as

$$\Delta_1^2 S = \Delta_1^2 S^\circ - R \ln \frac{c^2}{c^1} - R \ln \frac{\gamma^2}{\gamma^1} - RT \frac{\partial}{\partial T} \left(\ln \frac{\gamma^2}{\gamma^1} \right) \quad (20)$$

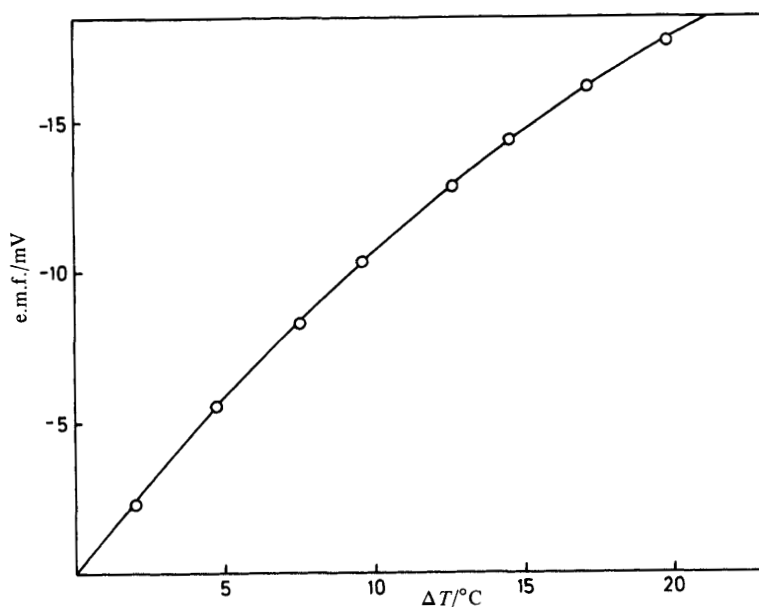
where S° is the standard value of the partial molar entropy. Unfortunately, no data are available for the standard entropy of transfer of TBA^+ between water and nitrobenzene.¹² In order to estimate this value, one can compare the values obtained for *N,N*-dimethyl-

Table 1. Values of $(E - E^\circ)/\text{mV}^a$

$\Delta T/^\circ\text{C}$			
4.7	9.6	14.5	19.8
-5.55	-10.20	-14.35	-18.0
-5.60	-10.20	-14.55	-17.6
-5.45	-10.40	-14.20	-17.5
-5.40	-10.40	-14.55	-17.5
-5.45	-10.40	-14.30	-17.6

$\Delta T/^\circ\text{C}$			
2	7.5	12.6	17.1
-2.25	-8.05	-13.10	-15.90
-2.30	-8.20	-12.80	-16.25
-2.30	-8.35	-12.90	-16.25
-2.25	-8.45	-12.90	-16.25
-2.30	-8.25	-12.75	-16.20

^a E is the e.m.f. of the cell shown in fig. 2 [$E = E(\text{hot}) - E(\text{cold})$].

**Fig. 3.** Thermo-e.m.f. of the water/nitrobenzene/water thermocouple illustrated in fig. 2.

formamide (DMF), which has similar physical properties to those of nitrobenzene [$\varepsilon_{\text{DMF}} = 36.71$, $\varepsilon_{\text{PhNO}_2} = 34.82$ and $(\partial\varepsilon/\partial T)_{\text{DMF}} = -0.178$, $(\partial\varepsilon/\partial T)_{\text{PhNO}_2} = -0.180$]. For DMF, enthalpy and entropy of transfer are available as shown by the recent IUPAC review compiled by Marcus.¹² ($\Delta H^\circ = 19 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 150 \text{ J K}^{-1} \text{ mol}^{-1}$). These two values give a Gibbs energy of transfer from water to DMF of $-23.7 \text{ kJ mol}^{-1}$, which

compares well with that obtained for the Gibbs energy of transfer from water to nitrobenzene, $-23.8 \text{ kJ mol}^{-1}$.¹³ Because the concentration of TBA^+ was low in the two immiscible phases of the thermocouple used, one can further assume that the entropy of transfer for the system studied can be approximated to the standard entropy of transfer.

It follows from eqn (19) that the Eastman entropy difference is negative and equal to *ca.* $-30 \text{ J mol}^{-1} \text{ K}^{-1}$. Since the heat of transport of TBA^+ in water is positive and is equal to $64.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ⁶ (under the assumption $*S_{\text{Cl}^-} = 2.05 \text{ J mol}^{-1} \text{ K}^{-1}$),¹⁴ it means that the Eastman entropy in nitrobenzene is equal to about half that in water.

Following Eastman's suggestions¹⁵ that heats of transport are related to reversible thermal effects occurring in the vicinity of the moving ion, we can assume that during the movement of the ion heat is liberated ahead of the ion and absorbed behind, as the entropy of solvent molecules falls when they are subjected to the ionic field. The present result therefore shows that a moving TBA^+ ion has a stronger structure-making effect in water than in nitrobenzene, which is a more randomly orientated solvent. Such an effect had been observed by Chakraborty and Lin,¹⁶ who showed that the Eastman entropies for very dilute solutions of alkali-metal chlorides were less positive in D_2O than H_2O .

Although the assumptions used to obtain the difference of Eastman entropy are very crude, the results obtained with the water/nitrobenzene/water thermocouple tend to show that heats of transport are smaller in solvents less structured than water.

All in all, it has been shown that the use of a new type of non-isothermal galvanic cell allows the direct measurement of the differences of transported entropy between two immiscible electrolyte solutions. However, in order to test the theories proposed for the modelling of heat of transport in solutions, good data for standard entropies of transfer are required.

A further conclusion of this work is provided by the thermodynamic analysis of this system which allows us to predict that a Peltier effect should be observed. If a current was imposed to flow through the isothermal junctions of the water/nitrobenzene/water thermocouple, then a heating up or cooling down should be noticed. Because in the system used, the current through the two liquid/liquid interfaces will be carried only by tetrabutylammonium, the Peltier heat would be given by eqn (18).

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