Sciences & Technologie – N°18, Décembre (2002), pp. 28-30.

THE EFFECT OF ALKALI-METAL HALIDES ON THE STRUCTURE OF GLYCEROL FROM VISCOSITY *B*-COEFFICIENT MEASUREMENTS

Reçu le 06/01/2001 – Accepté le 02/12/2002

Abstract

Viscosity *B*-coefficients in glycerol obtained at 25 °C for many salts by a rearrangement in the Jones-Dole expression are compared with those calculated applying existing theories, based on the model of hard-charged spheres moving in a solvent continuum. Specific agreement between theory and experiment was not generally good. While the results show that Einstein's relation can be applied to large aqueous ions, provided that the true volume-fraction of the ions in solution can be ascertained; this expression does not lead to accurate *B*-values in glycerol. For the ion-size dependence of the *B*-coefficient in aqueous solutions, Clark's theoretical predictions agree with experiments qualitatively, in the case of glycerol, however, the model shows limitations even for small ions, for which the dielectric friction theory is expected to be applicable. Finally, all the above theories give a positive *B*-coefficient, while experimental evidences showed that *B* could be negative.

Key words*: Viscosity B-coefficient, density, partial molar volume; electrolyte solutions; ionic friction theory; solvent-dipole relaxation.*

Résumé

Les coefficients de viscosité B dans le glycérol obtenus à 25°C pour plusieurs sels par un réarrangement de l'équation de Jones et Dole sont comparés avec ceux calculés en appliquant des théories existantes basées sur le modèle de sphères dures chargées se déplaçant dans un milieu liquide continu. Les résultats expérimentaux ne sont pas généralement en accord avec la théorie. Ces résultats montrent que la relation d'Einstein est applicable pour des ions larges dans un milieu aqueux, mais n'est pas valide dans le glycérol. Pour ce qui est de la dépendance des coefficients-B en milieu aqueux en fonction de la taille des ions, la relation de Clark est qualitativement en accord avec l'expérience, bien que dans le glycérol, ce modèle montre des limites, même pour des ions de petites tailles, où la théorie de la friction diélectrique est supposée être applicable. Finalement, toutes les théories citées précédemment donnent un coefficient-B positif, alors que des évidences expérimentales montrent que B peut aussi être négative.

Mots clés *: Coefficient de viscosité B, Volume molaire partiel, Solutions électrolytiques, Théorie de la friction ionique, Relaxation solvant-dipôle.*

A. HAMMADI
Département de Physique
Faculté des Sciences
Université de Mentouri
Constantine, Algérie

ملخص

عوامل اللزوجة B في الغليسرين المحصل عليها في 25°C لعدة أملاح مستعملين ترتيب لعلاقة "جونس ودول" قرنت مع تلك التي حسبت بتطبيق النظريات الحالية المستندة على نموذج الكرة المشحونة المتحركة في مذيب متسلسل. يلاحظ عامة عدم توافق نوعي بين النظرية والتجربة. بينما تبرز النتائج أن تطبيق علاقة "أنشتين" ممكن في حالة إيونات عريضة في وسط مائي؛فإن هذه العلاقة لا تعطي نتائج دقيقة في الغليسرين. أما في ما يخص تعلق العامل B بحجم الإيون، تنبأ "كلارك" النظري يتطابق نوعيا مع التجريبية في حالة محلول مائي، ولكن يظهر في الغليسرين نقائص حتى في حالة الإيونات الصغيرة أين تطبيق نظرية الاحتكاك الإيوني مؤكد عليه. في النهاية، تعطي كل النظريات السالفة عامل لزوجة موجب، بينما حقائق تجريبية تبين أن ممكن أن يكون B سالب.

الكلمات المفتاحية: *عوامل الزوجة B، نظرية الاحتكاك الإيوني، مذيب متسلسل.*

The *B*-coefficients of the Jones-Dole [1] empirical expression of the relative viscosities of electrolyte solutions as a function of concentration are important for a number of reasons.

(i) They are known to provide information concerning the solvation of the ions and their effects on the structure of the solvents in the near environment of the solute particles.

(ii) Because of the nature of the *B*-coefficients and their ion-additive properties, they may provide the key for the rationalization of a host of thermochemical data. This fact alone makes the current work timely.

If the *B*-coefficient of a given ion or a given electrolyte in various solvents [2] are compared, we observe that they have some relation to the molar volumes, V_Φ^∞, of the solvents. Taking for instance the solvents glycerol (V_Φ^∞/cm^3 mol^{-1} = 44.5), water (V_Φ^∞/cm^3 mol^{-1} = 45.4) and ethylene glycol (V_Φ^∞/cm^3 mol^{-1} = 46.6) and an electrolyte such as potassium iodide, the corresponding B /dm^3 mol^{-1} values are -0.178, -0.075 and 0.033 at 25 °C. Thus, glycerol, having the smallest molar volume V_Φ^∞, also generally exhibits the smallest *B*-coefficient.

Although it remains an open question how to derive *B*, this quantity was shown by Einstein [3] to be given by the equivalent quantity for suspensions of spherical macroscopic but very small particles. Einstein calculated the energy dissipated per unit time per unit volume by the resistance of the solvent, respectively the suspension, to the flow, and obtained therefrom the relationship of the viscosity of the suspension relative to the solvent. In a later paper, Clark [4] applied to viscosities the methods used by Zwanzig [5] for determining the contributions of dielectric relaxation to ionic conductivities. He assumed that the process of viscous flow depends upon solvent properties in much the same manner as ionic friction coefficients; there is an inverse dependence upon ionic radius.

It is the purpose of this paper to use previous viscosity and density measurement results [2] that have been obtained in glycerol with alkali-metal halides at 25 °C to test quantitative theories on the *B*-coefficients. The aim is to determine whether electrolyte solutions in glycerol can be described and explained using the semiempirical models that have had success with aqueous solutions, despite the fact that at 25 °C the viscosity of glycerol is nearly a thousand times greater than that of water. Glycerol is interesting among nonaqueous solvents because, like water, it is a hydrogen-bonded solvent with a high relative permittivity. It is thus natural to look for similarities in behaviour between the two solvents.

EXPERIMENTAL SECTION

Commercial glycerol, Aldrich gold label grade, quoted as 99.5 + % pure was further distilled under reduced pressure at 140 °C and 0.5 mm Hg. The salts (KCl, KBr, NaCl, and KI) used to prepare solutions in glycerol were Aldrich anhydrous gold label, quoted as 99.999 % pure. An ASTM 445 Technico Ubbelohde suspended bulb level viscometer, type VHB-590-170F, size 3 C was used for all viscosity measurements. Measurements with kinematic viscometers are associated with accurate determination of the density, and 25 ml Technico densitybottles type B5733 were used. All the experimental details-viscosity- and -density measurements, preparation and purity of the solutions, and temperature control have been presented previously [2, 6, 7].

RESULTS AND DISCUSSION

According to Einstein, the presence of large kinetic entities in a liquid enhance the viscosity η

$$\eta = \eta_0\,(1+2.5v)$$

where η_0 is the solvent viscosity and v is the volume fraction occupied by the spherical particles, v must be taken to include the volume of any solvent immobilised on the surface of the particle. This volume fraction v is expressed by

$$v = c\overline{V}$$

where c is the concentration in moles dm^{-3}, and $\overline{V}$ is the molar volume of the solute including attached solvent, in dm^3 mol^{-1}. Einstein's theory would successfully be used to describe the viscosity of electrolyte theory if $\overline{V}$ is assumed to be equal to the partial molar volume of the solvated solute V_Φ^∞. At higher concentrations the $A\sqrt{c}$ term in the Jones-Dole expression is very small in comparison with the Bc term, it can safely be neglected and since $v = c\,V_\Phi^\infty$, we finally obtain the expression

$$B_{\mathrm{EINST}} = 0.25[\,V_\Phi^\infty/(\mathrm{dm^3\,mol^{-1}})] \qquad (1)$$

Since previous experiments [2] have provided values for the apparent molar volumes, V_Φ^∞, they were put into Eq. (1).

Clark's calculations which takes into account both hydrodynamic and electrostatic interactions yielded an ionic *B*-coefficient, in SI units, of the form

$$B_{\mathrm{Clark}}^{\mathrm{ION}} = \left[S_H R^3 + S_D\,\frac{e^2(\varepsilon_s-\varepsilon_\infty)\tau}{4\pi\,\varepsilon_0\,\eta_0\,\varepsilon_S(3\varepsilon_s+2)R}\right]N_A \qquad (2)$$

where:
$S_H = 10\pi/3$, $S_D = 5/12$ for stick, $S_H = 4\pi/3$, $S_D = 2/3$ for slip.

Subscripts *H* and *D* refer to hydrodynamic disturbances and dielectric relaxation. N_A is the Avogadro constant, e is the proton charge, η_0 is the solvent viscosity, R is the ionic radius, ι is the dielectric relaxation time, and ε_S and ε_∞ are the static low- and -high frequency permittivities. The values of ε_S and ε_∞, η_0 and τ required in order to compute values of *B*-coefficient using eq. (2) were in glycerol 40, 4.2, 0.909 Pa.s, 1.12×10^{-9} sec, respectively [6]. The predicted *B*-coefficients at 25 °C obtained using Eq. (1) and (2) are shown in table 1, where for comparison we have also included data for aqueous solutions [4]. The data includes the values for salts involving large hydrophobic ions, e.g., tetraalkyllammonium iodides in glycerol and water at 25 °C [8]. Included also in table 1 are the experimental partial molar volume, V_Φ^∞, in cm^3 mol^{-1} that are involved in the relationship of the *B*-coefficient in Eq (1). A dash in column 3 and 4 means that V_Φ^∞ is not available for a satisfactory estimation of *B*.

Solvent	Partial molar volume V_Φ^∞	Salt B (experimental)		B (calculated)	
				EINSTEIN	CLARK
Glycerol	13.6	NaCl	0.463	0.034	0.031
	22.5	NaBr	0.360	0.056	0.034
	24.0	KCl	- 0.016	0.060	0.032
	32.9	KBr	- 0.107	0.082	0.035
	44.5	KI	- 0.178	0.110	0.041
	-	Et_4NI	- 0.680	-	0.130
	-	Pr_4NI	- 2.900	-	0.171
	-	Bu_4NI	- 1.900	-	0.211
Water	16.4	NaCl	0.079	0.041	0.071
	23.5	NaBr	0.053	0.059	0.073
	26.5	KCl	- 0.014	0.066	0.065
	33.7	KBr	- 0.049	0.084	0.067
	169.2	Et_4NBr	0.343	0.420	0.208
	185.3	Et_4NI	0.312	0.463	0.102
	250.7	Pr_4NI	0.843	0.627	0.175
	311.9	Bu_4NI	1.202	0.779	0.215

Table 1: Experimental and theoretical *B*-coefficients in dm^3 mol^{-1}, and partial molar volumes V_Φ^∞ in cm^3 mol^{-1} for salts in glycerol and water at 25 °C. Also included are the ionic crystallographic radii *R* in m.

The experimental values of the *B*-coefficients of 1:1 electrolytes consisting of small ions (i.e., not large hydrophobic ones) obtained at 25 °C by a rearrangement of the Jones-Dole expression are generally smaller than 0.1 dm^3 mol^{-1}. For many salts they are considerably smaller, e.g., *B*(KCl, glycerol) = -0.016 dm^3 mol^{-1}. For some salts they are negative, e.g., *B*(KI, glycerol) = -0.178 dm^3 mol^{-1}. For salts involving large hydrophobic ions in glycerol *B*-coefficients are commonly larger and almost always negative e.g., *B*(Et_4NI, glycerol) = 0.68, *B*(Pr_4NI, glycerol) = -2.9, and *B*(Bu_4NI, glycerol) = -1.9 dm^3 mol^{-1}, whilst in aqueous solutions *B*-coefficients are commonly larger and almost always positive e.g., *B*(Et_4NI, aq.) = 0.312, *B*(Pr_4NI, aq) = 0.843, *B*(Bu_4NI, aq.) = 1.202 and *B*(Et_4NBr, aq.) = 0.295 dm^3 mol^{-1}.

The B-coefficients obtained from experimental data were compared with those calculated applying relationships given as Eq. (1) and (2) for suspensions of spherical particles. A better agreement is achieved when the *B*-coefficient for aqueous solutions are related to the standard partial molar volumes V_Φ^∞, as it was the case with large aqueous tetraalkylammonium ions. As has already been noted, this is due to the presumption that major contribution to *B* arises from the volume of the ion in the solution, as if it were a nonelectrolyte and therefore obeying the Einstein relationship. However, B/V_Φ^∞ for such ions in glycerol is not constant and deviates from 2.5. Although it is accepted that the larger tetreaalkylammonium ions are practically unsolvated, the flexibility of the alkyl chains may cause them to have different shapes in different solvents, leading to departure from the Einstein relation in glycerol.

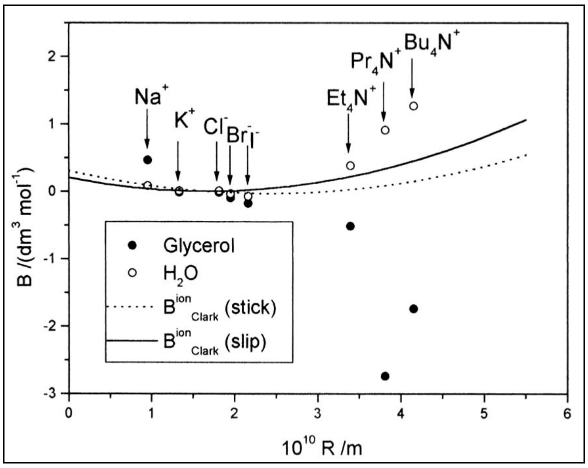

Figure 1: Ion size dependence of theoretical and experimental values of *B*-coefficients in glycerol (present work) and in water taken from Marcus and Jenkins (1995) at 25 °C.

In Figure 1, the predicted *B*-coefficients for perfect ''slipping'' (Full line) and ''sticking'' (dotted line) boundary conditions obtained using Eq. (2), are compared with the experimental values. The crystallographic radii *R* used are as follows (in angstrom units): $R(Na^+)$ = 0.95, $R(K^-)$ = 1.33, $R(Cl^-)$ = 1.81, $R(Br^-)$ = 1.95, $R(I^-)$ = 2.16, $R(Et_4N^+)$ = 3.39, $R(Pr_4N^+)$ = 3.81, $R(Bu_4N^+)$ = 4.15. While values (positive ones) of *B* calculated in the case of small ions in glycerol are very low, compared to experiment, even when the correction for ''slippage'' is applied; in water the agreement is generally good. The experimental *B*-coefficient in glycerol is much larger in the case of Na^+ (i.e., not large hydrophobic ion) and this observed maximum at sodium ion appears to be a real, unexplained phenomenon.

Finally, a comparison with previous work [7] need to be sought. The Zwanzig theoretical treatment of the solvent dipole relaxation effect was tested for the mobility of ions. The resulting conductance –viscosity products for the alkali-metal halides ions in glycerol and other solvents is illustrated in Fig. 2 as function of ionic crystallographic radii. The predictions to ionic mobilities for perfect ''slip'' conditions in glycerol and water are also given in the figure. One can see that there are similarities between Clark's calculations of *B* and Zwanzig's calculations of ionic conductivities λ_0; theoretical values are always less than the experimental ones.

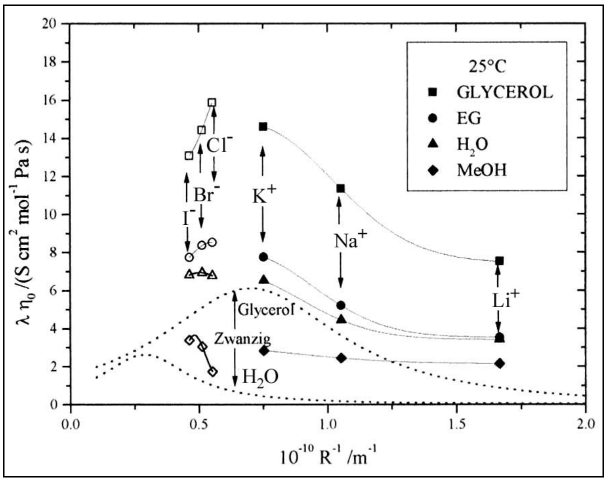

Figure 2 : Graphs showing the dependence of limiting ionic Walden product on the reciprocal of the ionic radius for ions in various solvents at 25 °C [7].

CONCLUSION

The *B*-coefficient depends on ion-solvent interactions and is related to the volumes of the ions, but so far in a theoretically inaccessible manner. The existing theories predict *B* to be always positive, while experimental evidences showed that *B* could be negative. Although the theories appears to be sound in water, they do not hold when the solvent is changed. Finally, a quantitative theory of viscosity of electrolytic solutions for the *B*-coefficient, valid for all solvents, which give a theoretical interpretation of the effects of ion-size, solvent on viscosity still awaits development.

REFERENCES

[1]- Jones G., Dole M., *J. Am. Chem. Soc.*, 51 (1929) 2950.
[2]- Hammadi A., Champeney D.C., *J. Chem. Eng. Data*, 43 (1998) 1004.
[3]- Einstein A., *Ann. Phys.*, 19 (1906) 289 ; 34 (1911) 591.
[4]- Clark G.J., *J. Chem. Phys.*, 65 (1975) 1403.
[5]- Zwanzig R., *J. Chem. Phys.*, 38 (1963) 1603; 52 (1970) 3625.
[6]- Hammadi A., Champeney D.C., *J. Sol. Chem.*, 28 (1999) 21.
[7]- Hammadi A., Champeney D.C., J. *Chem. Eng. Data*, 45 (2000) 1021.
[8]- Jenkins H., Donald B. Marcus, *Chem. Rev.*, 95 (1995) 2695.☐