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LIQUID DIFFUSIVITIES IN THE GLYCOL-WATER SYSTEM

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Submitted to Journal Physical Chemistry

UCRL-16622

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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February 1966

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by

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ABSTRACT

Mutual diffusion coefficients are reported for the system ethylene glycol-water over the entire range of compositions at temperatures ranging from 25 to 70°C. Differential coefficients were obtained by the use of diaphragm cells and a differential interferometer. It was found that the group $D\eta/T$ is temperature independent and varies linearly with the mole fraction of glycol present. The theoretical implications of these results are discussed briefly.

While many binary liquid diffusivity values have been measured, they have been mainly restricted to room temperature and in many cases only a value at high dilution is known. Our ability to predict the effect of concentration level upon diffusivity is limited to quite simple systems. Corrections for nonidealities have been mainly confined to instances where regular solution theory is postulated[1] and the activity coefficient is used to alter the prediction. The activity coefficient correction factor has been shown to effect an overcorrection in many cases of non-ideal solutions, both where there are associative forces at play and where there are no associative forces.[2,3] Irani and Adamson[4] have endeavored to show that for associating solutions one must consider clustered groupings rather than a true random binary in correlating diffusivity data.

The ethylene glycol-water system presents an opportunity to study an associated solution where the molecules are of quite different sizes and where there is an order of magnitude change in viscosity across the concentration range. Vapor pressure data for this system[5] show that it follows Raoult's Law closely throughout the temperature range of interest. A system of this type should provide a unique test of the existing theories.

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1. Bearman, R. J., J. Phys. Chem. 65, 1961 (1961).
2. Bidlack, D. L. and D. K. Anderson, J. Phys. Chem. 68, 206, 3790 (1964).
3. Anderson, D. K., J. R. Hall and A. L. Babb, J. Phys. Chem., 62, 404 (1958).
4. Irani, R. R. and A. W. Adamson, J. Phys. Chem. 64, 199 (1960).
5. Curme, G. O., and Franklin Johnston, Glycols, Reinhold Publishing Company, New York, 1952.

Two previous studies of the glycol-water system have been reported. One study reports a single value for ethylene glycol at high dilution in water at 15°C.[6] The other investigation covers a range of compositions at 20°C. and provides high dilution values at 25, 30 and 40°C.[7] The present experiments were designed to complete and extend the previous data.

In correlating liquid diffusivity data most workers have included the effect of temperature. However most of the data which exist for various systems at the present time are for the temperature range 15 to 40°C. It was therefore of some interest to attempt to extend this rather narrow range in order to place the temperature effect upon a stronger foundation.

Experimental

Diffusion measurements were carried out in a group of glass diaphragm cells. The cells were of the horizontal type described by Holmes, et. al.[8,9] The two solution compartments are horizontally opposed across a vertical fritted glass diaphragm. The temperature bath and other auxiliary equipment are also described by Holmes, et. al. The cell constants (β) were obtained in the present work by calibration with 0.1 N. KCl solutions. It is interesting to note that the constants found by Holmes for some

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6. Rossi, C., E. Bianchi, and A. Rossi, J. chim. Phys. 55, 93 (1958).
7. Garner, F. H. and P. J. M. Marchant, Trans. Inst. Chem. Engrs. (London) 39, 397 (1961).
8. Holmes, J. T., U. S. Atomic Energy Comm. Report UCRL-9145 (1960).
9. Holmes, J. T., C. R. Wilke and D. R. Olander, J. Phys. Chem. 67, 1469 (1963).

of the same cells several years earlier were almost identical to those found in this study, in spite of the fact that his calibration was carried out with 0.2 N. HCl solutions. Temperatures in the surrounding bath were controlled to $\pm$ 0.05°C in all cases. A Zeiss differential interferometer was used to analyze the difference in concentration between the solutions on either side of the diaphragm cells.

The classical diaphragm cell equation[10] was used to analyze the data:

$$\log_{10}\left[\frac{\Delta\rho_{1i}}{\Delta\rho_{1f}}(1-\lambda/6)\right] = \beta Dt(1-\lambda/6) \qquad (1)$$

The term $(1-\lambda/6)$ is a correction for finite holdup in the frit which was first proposed by Barnes.[11]

The two liquids used were distilled water and reagent grade ethylene glycol. It was found necessary to degas both of these before mixing the solutions. The solutions on either side of a cell typically differed in concentration by 1.5 weight %. The use of the differential interferometer made it possible to measure concentration differences of this size to an accuracy of 0.15% of the total difference in concentration. It is necessary to employ small concentration differences when one is dealing with horizontal diaphragm cells and with a solution of markedly varying density. When the densities of the solutions on either side of the diaphragm differ greatly, bulk flow caused by pressure gradients

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10. Gordon, A. R., Ann. N. Y. Acad. Sci. 46, 285 (1945).

11. Barnes, Colin, Physics 5, 4 (1934).

across the vertical diaphragm tends to provide apparent values of diffusivity which are far higher than the molecular values.

At the start of a run the entire cell was filled with the water-rich solution and allowed to stand in the bath for several hours. This solution was then removed from one side of the cell, and after several washings with the glycol-rich solution this side of the cell was filled with the latter solution. A run normally lasted two to three days. Since refractive index is a linear function of concentration over small ranges in concentration, the ratio of the interferometer readings for the initial and final concentration differences between compartments could be used directly in the left hand side of Equation 1.

Results

The results of this experimental program are presented in Table 1. The reported diffusivities are based upon the currently prevalent Chapman-Cowling definition,[12] by which

$$D = -j_1/\rho \nabla w_1 \qquad (2)$$

At constant temperature and either at constant pressure or for incompressible fluids, this definition is equivalent to

$$D = -j_1^o/\nabla \rho_1 \qquad (3)$$

Since the diaphragm cell configuration corresponds closely to no net volume flux across the diaphragm, Equation 3 leads directly to Equation 1.

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12. Lightfoot, E. N. and E. L. Cussler, Jr., Chem Eng. Prog. Symposium Series 65, No. 58, 66 (1965).

describe the data. For example, in the present case the factor containing the activity is unity; hence the product of the diffusivity and viscosity should be a linear function of mole fraction. Figures 1, 2, and 3 show the data plotted in this way for the three temperatures for which data were available. The viscosity data are taken from the book by Curme and Johnston.[5] For comparison with Equation 4, D_1^{∞} is taken to be the experimental value at 0.7 weight percent glycol. A least squares analysis indicates that a straight line fits the data well. The standard deviation in the slope is less than 5%; however the slope in all cases is about 50% higher than predicted by Equation 4.

The data of Figures 1, 2 and 3 appear to be best correlated by an equation originally suggested by Roseveare, Powell and Eyring[13] on a semi-empirical basis:

$$D\eta = \left(x_1 D_2^{\infty}\eta_1 + x_2 D_1^{\infty}\eta_2\right)\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T,P} \qquad (5)$$

Two experimental values of diffusivity are required for Equation 5 rather than the single value required for Equation 4. Equation 5 may also be obtained from Equation 12b given by Bearman,[1] using Bearman's prediction that $D_1\eta$ and $D_2\eta$ (his nomenclature) should be independent of concentration. The agreement of the present data with Equation 5 is remarkable in view of the fact that the viscosity varies by a factor of 12 to 17 and the diffusivity varies by a factor of 3 to 5 across the range of compositions at a given temperature.

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13. Roseveare, W. E., R. E. Powell, and Henry Eyring, J. Appl. Phys. 12, 669 (1941).

Equation 5 also agrees well in general with the data of Caldwell and Babb[14] for the systems benzene-CCl_4, chlorobenzene-bromobenzene and toluene-chlorobenzene and with the data of Bidlack and Anderson[2] for hexane-CCl_4, hexane-dodecane, hexane-hexadecane and heptane-hexadecane. Equation 4 agrees reasonably well with the Caldwell and Babb data where the molal volumes are nearly equal, but the Bidlack and Anderson data show a lack of agreement with Equation 4 similar to that found for glycol-water. For the hexane-CCl_4 system, Equation 4 predicts a substantial decrease in $D\eta$ with increasing mole fraction CCl_4, while the opposite is found experimentally. Hence, the use of the condition $D_1^{\infty}\eta_2/D_2^{\infty}\eta_1 = v_2/v_1$ (or $D_1/D_2 = v_2/v_1$) to bring about the transformation from Equation 5 to Equation 4 appears not to be experimentally justified in most cases. As pointed out in the introduction, Equation 4 also can fail seriously in cases where the two components of a solution differ markedly in polarity.[3]

An activation energy for diffusion may be found by plotting the natural logarithm of diffusivity as a function of the reciprocal of absolute temperature. The best least squares fit of the data produced a standard error in the resulting activation energy of less than 10%. Figure 4 shows the variation of activation energy with weight fraction. When this curve is compared with the one presented in the work of Garner and Marchant[7] for water-propane 1-2 diol, a similarity of shape is evident. As expected the larger molecule presents a higher diffusion barrier. A good discussion of the interpretation of such a plot is given by Garner and Marchant.

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14. Caldwell, C. S. and A. L. Babb, J. Phys. Chem., 60, 51 (1956).

Most of the classical theories for diffusivity at infinite dilution postulate that the group $D\eta/T$ is a constant. Recently Olander[15] has shown, from a generalization of the Eyring theory, that this may not generally be the case. Only identical molecules can be expected to have similar free energies of activation for both diffusion and viscosity, hence one could expect the grouping $D\eta/T$ to be a function of temperature. Figure 5 shows the correlation of $D\eta/T$ and temperature. While there is a certain amount of scatter in the data, the conclusion must be that no trend with respect to temperature is discernible.

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15. Olander, S. R., A.I.Ch.E. Jour. 9, 207 (1963).

Acknowledgments

This work was performed under the auspices of the United States Atomic Energy Commission. Thanks is due D. L. Osterholt for his patient laboratory assistance.

Notations

a	Solute activity
$\Delta\rho$	Difference in concentration across the diaphragm in the diaphragm cell, gram/cm.^{3}
ρ	Concentration, gram/cm.^{3} With no subscript, ρ = density.
D	Diffusion coefficient, cm.^{2}/sec.
E_{act}	Activation energy for diffusion, kcal/g.mole
j	Mass flux relative to mass average velocity, grams/cm^2/sec.
j^o	Mass flux relative to volume average velocity, grams/cm^2/sec.
P	Pressure, atmospheres
T	Temperature, ^oK
t	Temperature, ^oC
v	Molar volume of pure component, cm^3/gram mole
w	Weight fraction
x	Mole fraction
β	Cell constant
θ	Total time, sec.
λ	Volume of frit/volume of one cell chamber
η	Viscosity, cp.

Subscripts

i	initial
f	final
1,2	chemical component number

Superscripts

∞	at infinite dilution

Table 1

Experimental Diffusion Coefficients x 10^5
(Cm^2/Sec.)

Temperature (°C) \ Wt% Glycol	0.70	22.5	43.4	62.7	82.0	99.2
25	1.16_0	0.93_3	0.71_0	0.50_9	0.36_0	0.24_3
40	1.71_2	1.17_7	0.95_4	0.75_1	0.56_9	0.50_0
55	2.25_6	1.80_2	1.40_1	1.15_5	0.93_8	0.70_6
70	2.75	2.20	----	----	----	1.13

Captions for Figures 1 to 5 of UCRL #16622

Figure 1. $D\eta$ as a function of mole fraction ethylene glycol at 25°C
---- Best fit of data, _____ Equation 4

Figure 2. $D\eta$ as a function of mole fraction ethylene glycol at 40°C
---- Best fit of data, _____ Equation 4

Figure 3. $D\eta$ as a function of mole fraction ethylene glycol at 55°C
---- Best fit of data, _____ Equation 4

Figure 4. Activation energy as a function of weight fraction ethylene glycol.

Figure 5. $D\eta/T$ as a function of temperature. ▲ - present study, o - Garner and Marchant, ⊡ - Rossi et al. Arrow indicates 40°C data of Garner and Marchant.

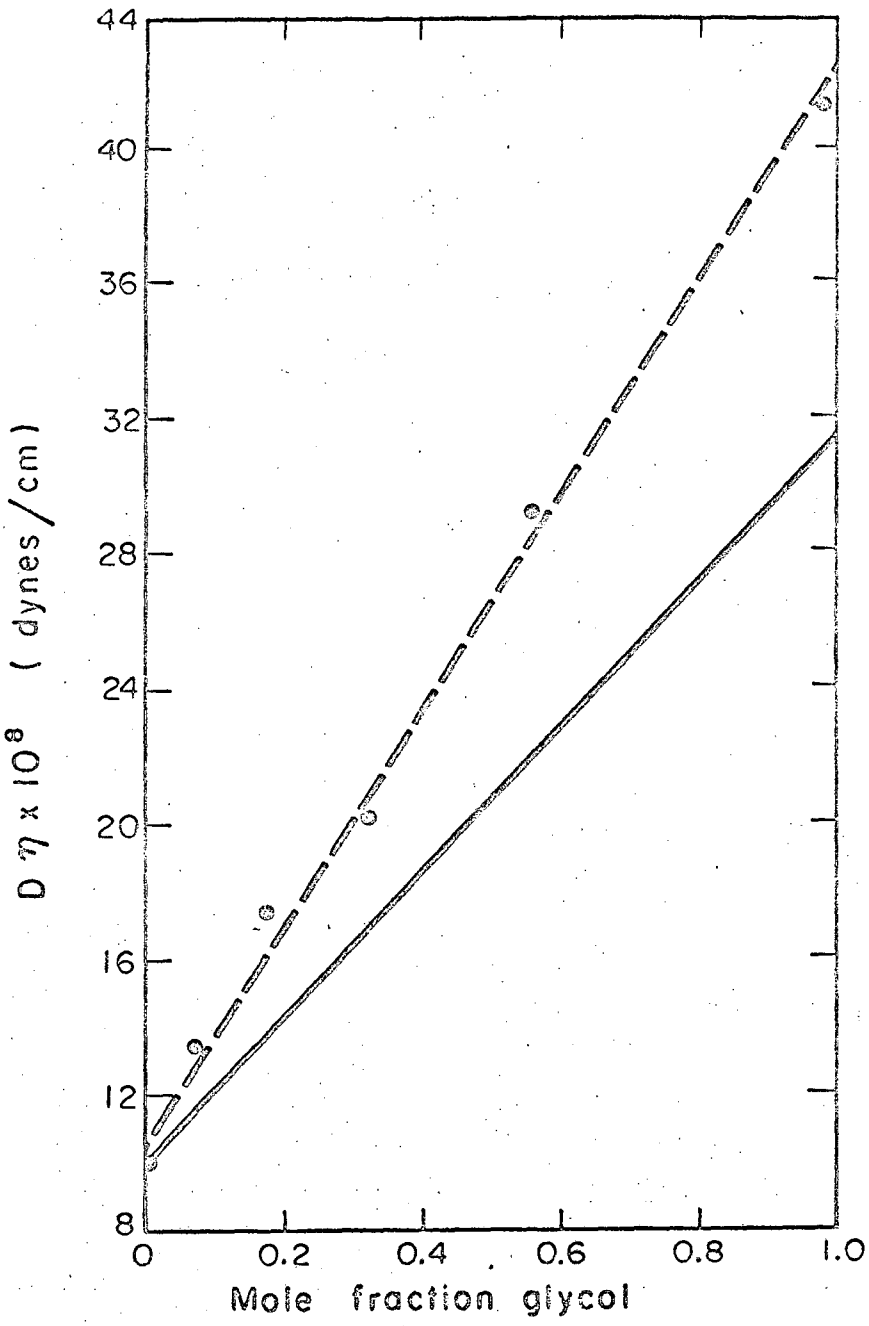

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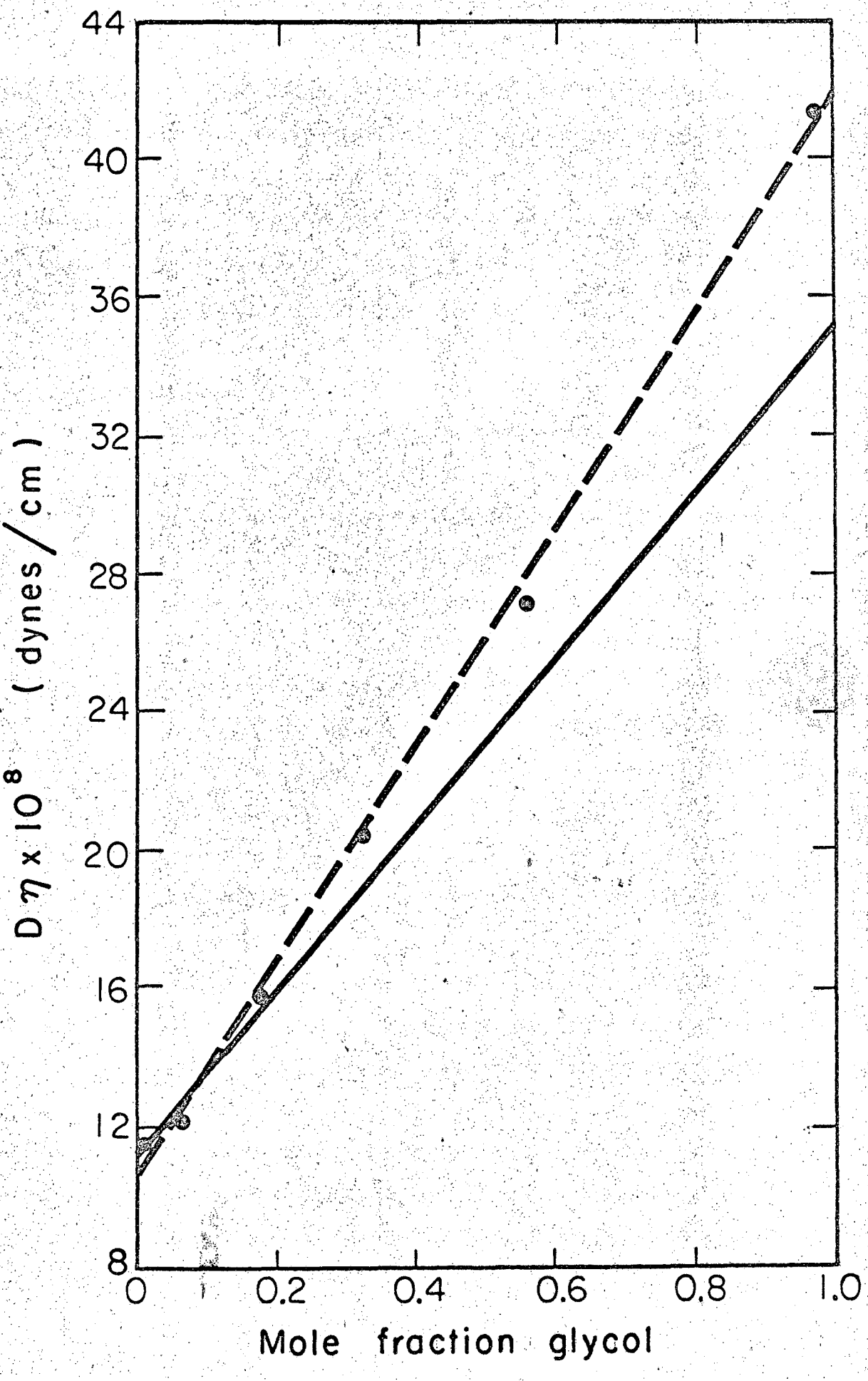
Fig. 1


44
40
36
32
28
24
20
16
12
8
0
0.2
0.4
0.6
0.8
1.0
D η x 10⁸ (dynes / cm)
Mole fraction glycol

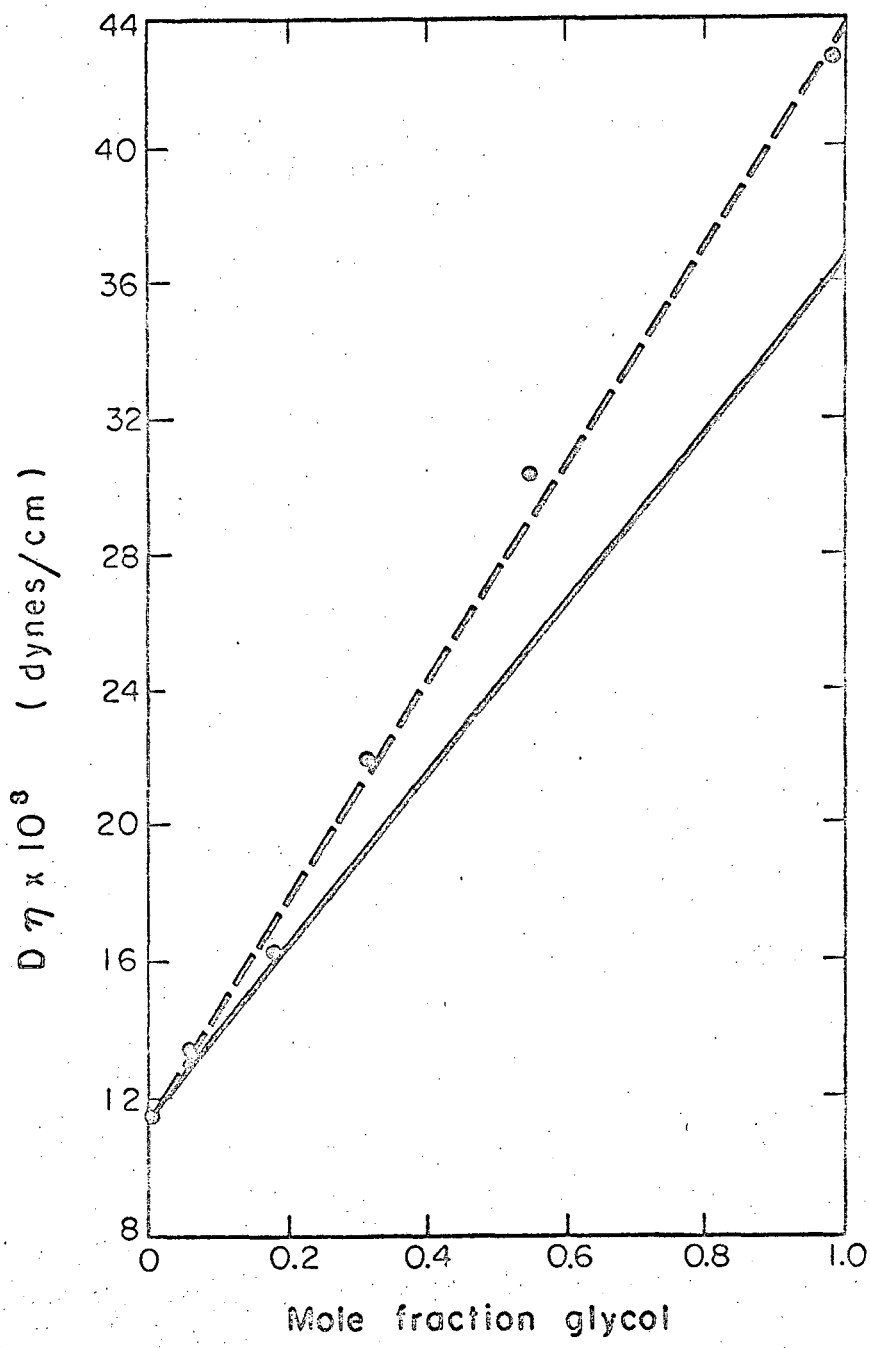


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Fig. 3

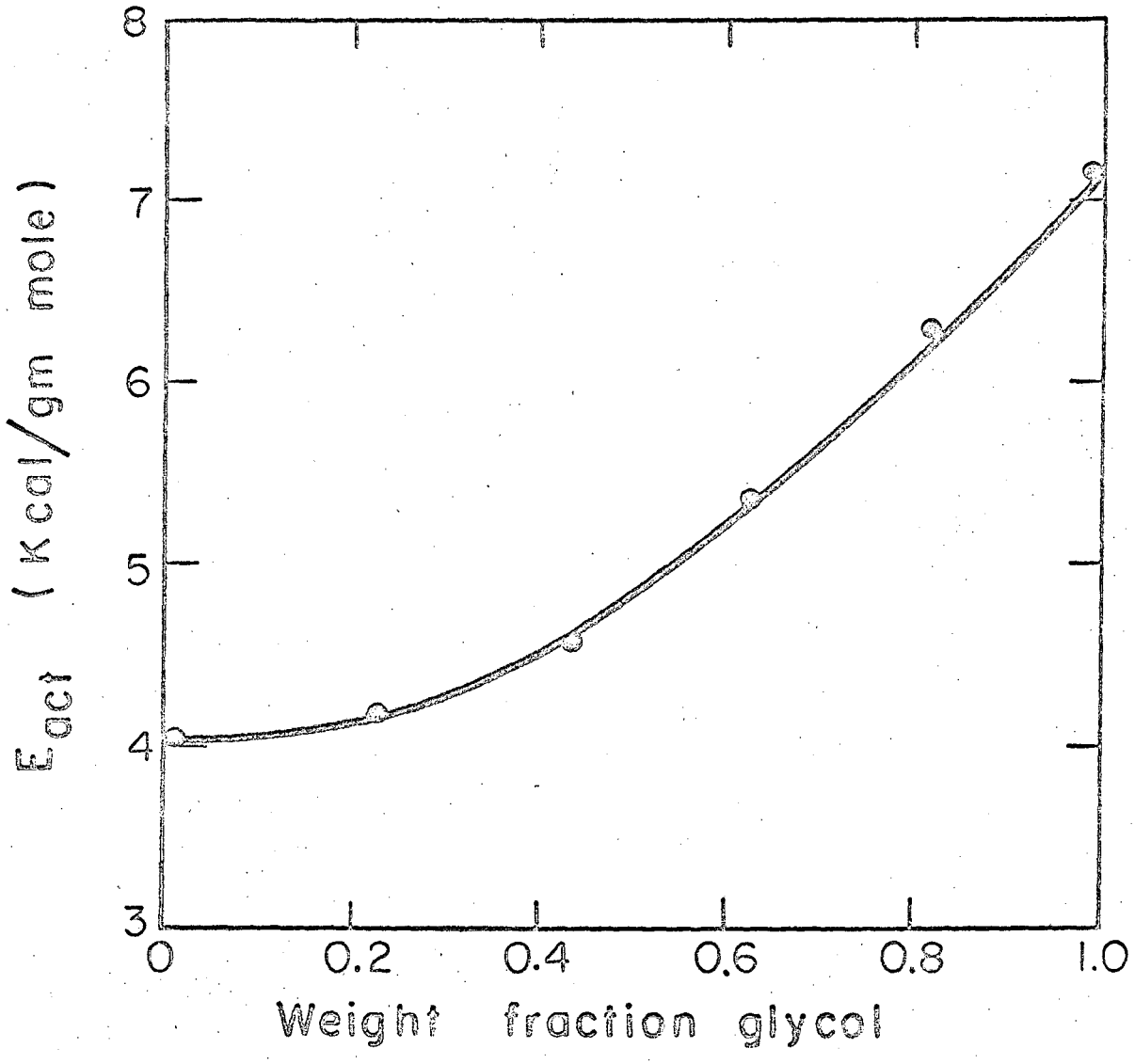

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Fig. 4

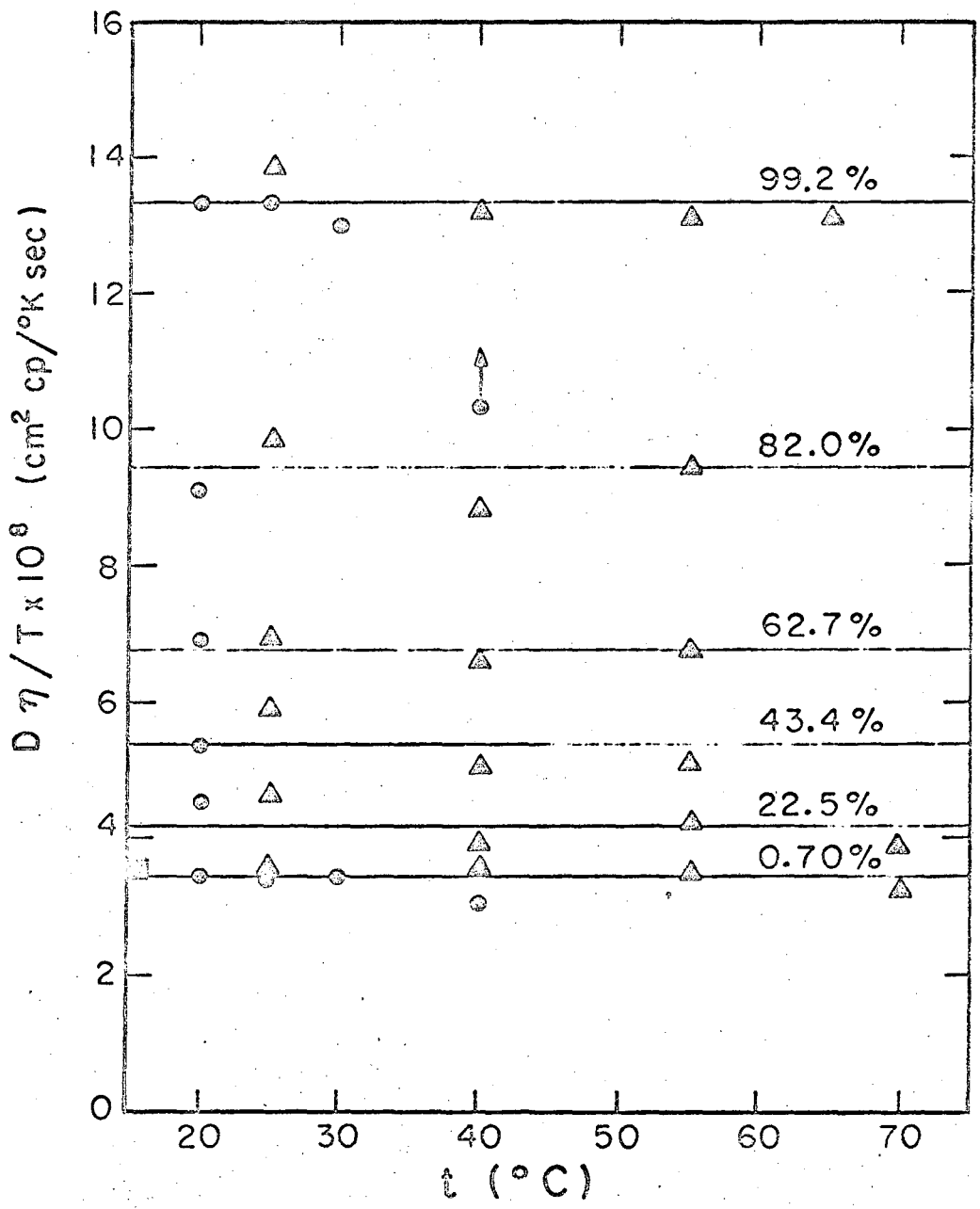

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Fig. 5

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