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Note

MOLAR EXCESS GIBBS FREE ENERGIES OF MIXTURES OF ETHANOLAMINES AND WATER

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Thermodynamic information about the vapor—liquid equilibria of systems containing water and ethanolamines is needed in the design and optimization of important industrial processes. This knowledge is also useful in the investigation of some phenomena such as the thermal conversion of ethanolamines or their complexation reactions with metals.

Physico-chemical investigations involving aqueous solutions of ethanolamines are scarce, and sometimes contradictory, in the literature. It has been stated [1] that the system diethanolamine—water obeys Raoult's law. However, there have been studies [2] indicating departure from ideal behavior for this system.

The purpose of this work was to determine the molar excess Gibb's free energies of the systems formed by water and the ethanolamines.

EXPERIMENTAL

Reagent grade ethanolamines were purified by means of distillation under reduced pressure. The pure chemicals had melting points equal to 10.4, 27.8 and 20.4°C, respectively, for monoethanolamine, diethanolamine and triethanolamine.

The experiments were performed using an apparatus recently described [3]. It consists of a still with continuous circulation of the vapor and liquid phases. The still is implemented with a Cottrell pump which delivers a stream of liquid and vapor on the thermometer well. Temperatures were measured with certified mercury thermometers with a precision of ±0.05°C. Samples from the condensate and the boiling liquid were withdrawn at the steady state corresponding to the thermodynamic equilibrium. The composition of these samples was determined by means of refractive index measurements, except for the binary diethanolamine—triethanolamine which was analysed by gas chromatography [4].

Isobaric vapor—liquid measurements were performed for the six binary pairs formed by water and the three ethanolamines. The pressures chosen for obtaining the data of each binary pair were somewhat variable due to experimental convenience and were around 90 mm Hg.

RESULTS AND DISCUSSION

Activity coefficients were calculated from the experimental data according to procedures given in the literature [5] and were used for a specific purpose [6]. Values of the molar excess Gibbs free energies, g^E, were then obtained from the relationship

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

where R is the gas constant, T is the absolute temperature and γ_1 and γ_2 represent the activity coefficients.

Figures 1 and 2 show the behavior of g^E as a function of composition and indicate negative deviations from ideality for all the systems studied. The departure from ideality is twice as large for the aqueous solutions. The values of g^E were fitted to the Wilson equation [7] with the help of a multiparametric curve-fitting program [8]. The standard deviations of the fits were typically 5% except for water—diethanolamine and water—triethanolamine where slightly larger deviations were observed.

The energy term $(\lambda_{ij} - \lambda_{ii})$ of the Wilson equation is closely related to the difference in cohesive energy between and i—j pair and an i—i pair. To a good approximation, this term is independent of temperature over a modest temperature range. The parameters λ_{ij} and λ_{ij} are negative because, in the liquid phase, the potential energy is always less than that of an ideal gas, whose

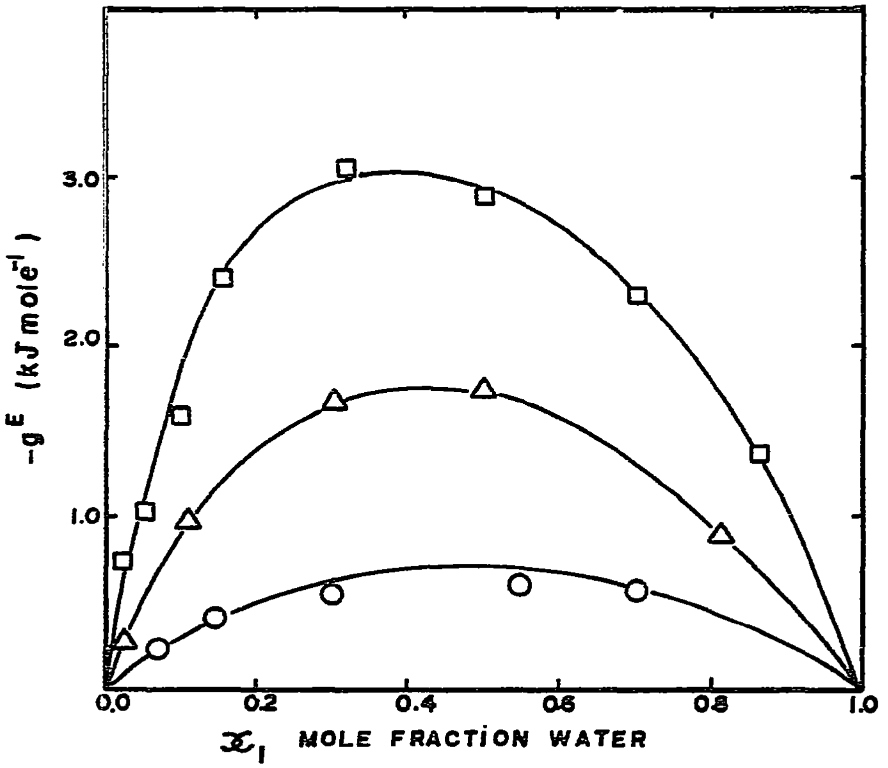

Fig. 1. Molar excess Gibbs free energy of the systems water—monoethanolamine (○), water—diethanolamine (△) and water—triethanolamine (□).

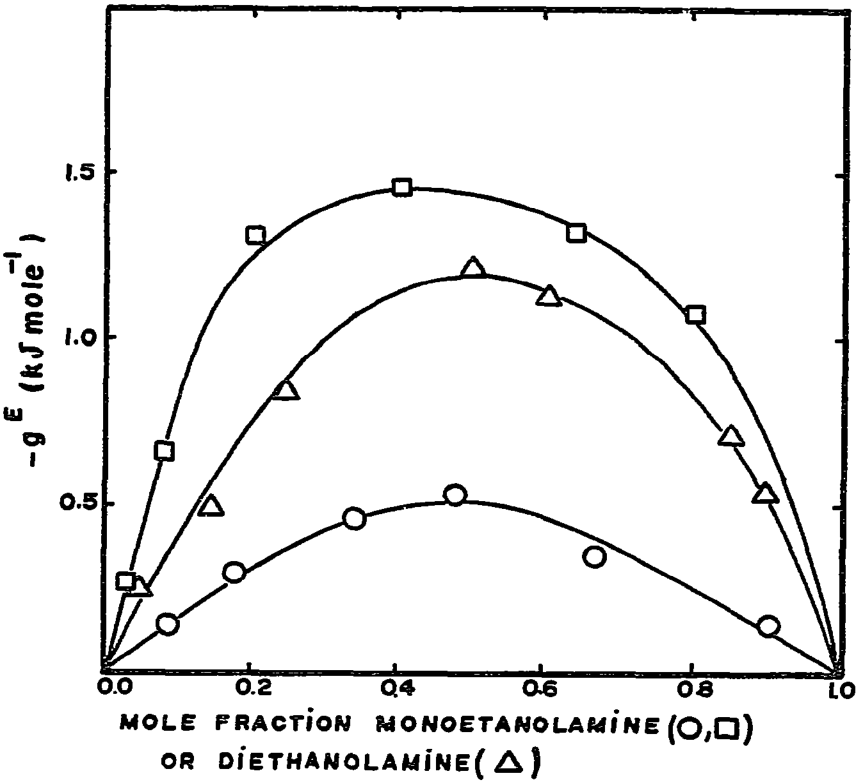

Fig. 2. Molar excess Gibbs free energy of the systems monoethanolamine—diethanolamine (○), monoethanolamine—triethanolamine (□) and diethanolamine—triethanolamine (△).

potential energy is zero. The values of these parameters can be interpreted in terms of the relative magnitudes of the interaction energies between the various pairs of molecules. A diagram representing these relative magnitudes is shown in Fig. 3.

It seems possible to conclude that the interactions between two molecules of water are the strongest of these systems, whereas the cohesive energy for triethanolamine—triethanolamine is the weakest. Also, the intermolecular energies in aqueous solutions of ethanolamines (λ_{12}, λ_{13}, λ_{14}) are stronger than those found for binary solutions including only ethanolamines (λ_{23}, λ_{24}, λ_{34}). This fact may be explained by the formation of hydrogen bridges between water and ethanolamine molecules. The precision of the data does not warrant a definite conclusion about the relative magnitudes of the interaction energies in solutions of different ethanolamines. However, the order given in Fig. 3 seems to be reasonable.

ACKNOWLEDGEMENT

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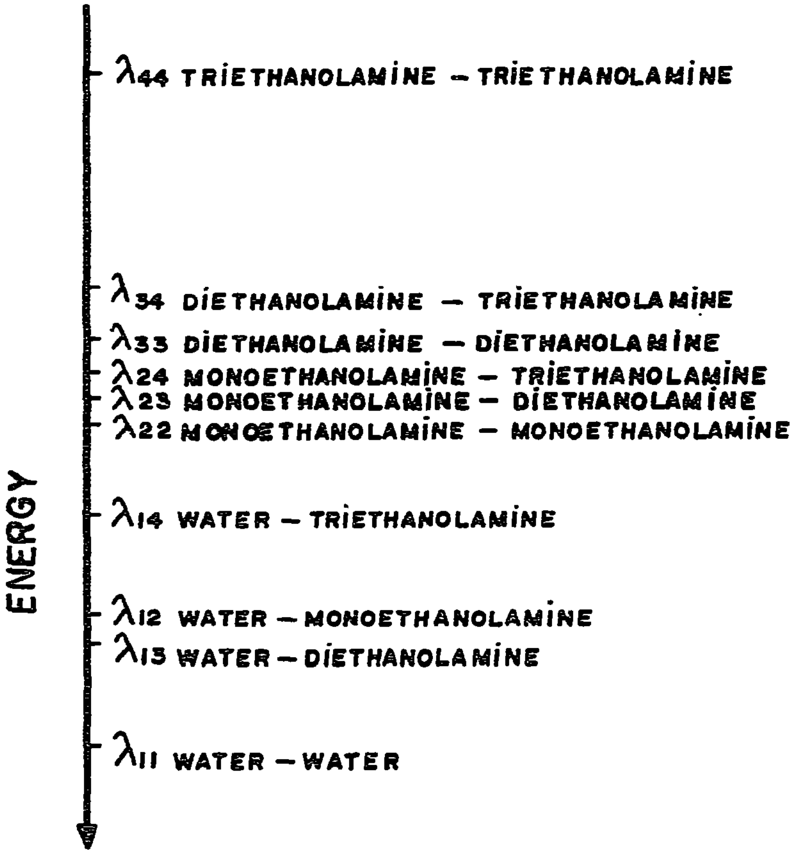

Fig. 3. Relative magnitudes of the interaction energies between the various pairs of molecules.

REFERENCES

1 N.B. Matin, S.M. Danov and R.V. Efremov, Kinet. Katal., 10 (1969) 749.
2 V.V. Danilov, I.G. Martinson and A.A. Ravdel, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol., 17 (1974) 140.
3 W.A. de Oliveira, A.F. Marconsin, A.P. Chagas and P.L.O. Volpe, Thermochim. Acta, in press.
4 R. Piekos, K. Kobyeczyk and J. Grzybowski, Ann. Chem., 47 (1975) 1157.
5 T. Boublik and G.C. Benson, Can. J. Chem., 47 (1969) 539.
6 Project UNICAMP-CODETEC No. TA 011/78.
7 G.M. Wilson, J. Am. Chem. Soc., 86 (1964) 127.
8 L. Meites, The General Multiparametric Curve-Fitting Program CFT4, Computing Laboratory, Department of Chemistry, Clarkson College of Technology, Potsdam, NY, 1976.