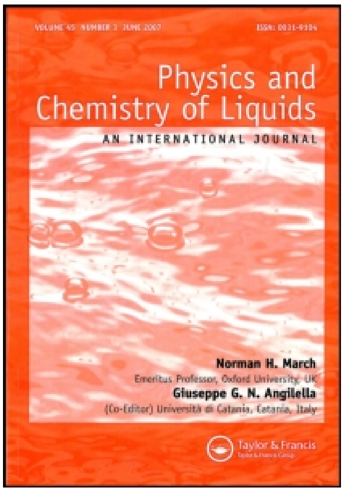

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Excess Isentropic Compressibilities of Binary Mixtures of N, N-Dimethylformamide with n-Alcohols at 303.1 5 K

William E. Acree Jr.[a]
[a] Department of Chemistry, Kent State University, Kent, Ohio, USA

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Excess Isentropic Compressibilities of Binary Mixtures of *N*,*N*-Dimethylformamide with *n*-Alcohols at 303.15 K

WILLIAM E. ACREE, Jr.

Department of Chemistry, Kent State University, Kent, Ohio 44242 (*USA*)

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An equation is given for the isentropic compressibility of an ideal binary solution and is used to calculate excess isentropic compressibilities of binary mixtures of *N*,*N*-dimethylformamide with methanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. The results of these calculations indicate that all five binary systems exhibit negative deviations from ideality contrary to the earlier calculations of Rao and Reddy.

KEYWORDS isentropic compressibility, ideal solution, binary mixtures of *N*,*N*-dimethylformamide and *n*-alcohols.

In a recent publication appearing in this journal, Rao and Reddy[1] calculated the excess isentropic compressibilities of binary *N*,*N*-dimethylformamide + *n*-alcohol mixtures as

$$K_s^{ex} = K_s - K_s^{ideal} \tag{1}$$

the difference between the observed isentropic compressibility and that of an ideal solution, K_s^{ideal}. The isentropic compressibility of the ideal solution was represented as

$$K_s^{ideal} = X_1 K_{s,1}^0 + X_2 K_{s,2}^0 \tag{2}$$

the mole fraction average of the isentropic compressibilities of the pure liquids $K_{s,i}^0$. While many thermodynamic and physical properties of an ideal solution are correctly described by mole fraction averages, the isentropic compressibility is not one of these properties.

The isentropic compressibility of any solution is related to the isothermal compressibility K_t by

$$K_s = K_t(C_v/C_p) \tag{3}$$

$$K_s = -(\partial \ln V/\partial P)_S \tag{4}$$

$$K_t = -(\partial \ln V/\partial P)_T \tag{5}$$

the ratio of heat capacities at constant volume and pressure, which are themselves related through

$$C_p - C_v = \alpha^2 VT/K_t \tag{6}$$

the coefficient of thermal expansion, $\alpha = (\partial \ln V/\partial T)_p$. The isothermal compressibility of an ideal binary solution can easily be shown to equal the volume fraction (ϕ_i) average of the isothermal compressibilities of the two pure liquids

$$K_t^{\text{ideal}} = \phi_1 K_{t,1}^0 + \phi_2 K_{t,2}^0 \tag{7}$$

and the isobaric heat capacity to equal the mole fraction average of the heat capacities of the pure liquids

$$C_p^{\text{ideal}} = X_1 C_{p,1}^0 + X_2 C_{p,2}^0 \tag{8}$$

Combination of Eqs 3–8 gives the following expression for the isentropic compressibility of an ideal binary solution

$$K_s^{\text{ideal}} = \phi_1\{K_{s,1}^0 + TV_1^0(\alpha_1^0)^2/C_{p,1}^0\} + \phi_2\{K_{s,2}^0 + TV_2^0(\alpha_2^0)^2/C_{p,2}^0\}$$
$$- T[X_1V_1^0 + X_2V_2^0][\phi_1\alpha_1^0 + \phi_2\alpha_2^0]^2/[X_1C_{p,1}^0 + X_2C_{p,2}^0] \tag{9}$$

which no way resembles a mole fraction average of the individual $K_{s,i}^0$, except in the very special case when the molar volumes, isobaric heat capacities, and isobaric thermal expansivities of both components are identical. It should be noted that Eq. 9 is identical with equations derived by Bertrand and Smith[2] and Benson and Kiyohara.[3,4]

In Table I, I compare the excess isentropic compressibilities as calculated by Rao and Reddy,[1] using Eqs 1 and 2, to those values calculated from Eqs 1 and 9 for binary mixtures of *N,N*-dimethylformamide with methanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. Numerical values of the isobaric heat capacities and thermal expansivities, at or near 303.15 K, were taken from the literature.[4–6] Most noticeable in this comparison is the fact that all five binary systems exhibit negative deviations from ideality contrary to the earlier calculations of Rao and Reddy.

TABLE I

Excess isentropic compressibilities of binary *N*,*N*-dimethylformamide + *n*-alcohol systems

X_{DMF}	K_s (TPa^{-1})	K_s^{ex} (TPa^{-1}) Eqs 1 and 2	K_s^{ex} (TPa^{-1}) Eqs 1 and 9
DMF + Methanol			
0.0773	917	− 80	− 48
0.2072	779	− 147	− 80
0.3984	648	− 174	− 89
0.4461	625	− 171	− 85
0.5176	600	− 157	− 74
0.5860	573	− 146	− 69
0.6935	550	− 111	− 47
0.7376	537	− 100	− 43
0.8174	520	− 73	− 32
DMF + 1-Propanol			
0.1492	806	− 26	− 25
0.1771	791	− 30	− 28
0.3107	717	− 51	− 48
0.3878	682	− 55	− 53
0.4898	640	− 57	− 54
0.5904	615	− 42	− 39
0.6929	574	− 42	− 40
0.7704	552	− 33	− 32
DMF + 1-Butanol			
0.1349	746	− 7	− 13
0.2148	720	− 10	− 18
0.3711	663	− 20	− 32
0.4450	638	− 22	− 37
0.5684	600	− 24	− 37
0.6484	578	− 21	− 34
0.7505	553	− 15	− 27
0.8261	536	− 10	− 18
0.8581	527	− 9	− 17
DMF + 1-Pentanol			
0.1928	719	4	− 10
0.2645	703	6	− 10
0.3416	679	7	− 16
0.4478	653	8	− 16
0.5154	636	10	− 15
0.6484	597	8	− 17
0.7005	584	8	− 14
0.8958	526	4	− 7
DMF + 1-Hexanol			
0.1748	694	− 7	− 23
0.2211	684	− 5	− 24
0.3532	659	3	− 24
0.4574	638	8	− 23
0.5029	628	10	− 22
0.6819	589	15	− 15
0.7044	584	16	− 13
0.8083	556	14	− 9
0.9041	529	11	− 3

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